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THE NANOSTRUCTURE STUDY ON THE MECHANISM OF LIME STABILISED SOIL

(KAJIAN STRUKTURNANO KEATAS MEKANISMA PENSTABILAN KAPUR)

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ABSTRACT

The poor engineering properties of clayey soils can be altered through chemical stabilization, resulting in a material suitable for construction purposes. The effect of calcium-based stabilizers on the geotechnical properties of soils has been reported by many researchers. However, the amount of literature available on the micro-structural, molecular, and leaching characteristics of lime and in particular phosphoric acid stabilized soils has been rather limited. In this thesis, two soil types comprised mainly of montmorillonite and kaolinite minerals (i.e., Green Bentonite and White Kaolin) and two tropical soils (Laterite Clay and Pink Soil) were chosen. The primary objective of this investigation was to elucidate the possible mechanisms by which different soils are modified in a highly acidic and basic environment. This was achieved by studying the changes induced in soil-stabilizer matrix using X-ray Diffractometry (XRD), Energy Dispersive X-ray Spectrometry (EDAX), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR), Cation Exchange Capacity (CEC) and BET surface area analysis. Also, in order to correlate the structural evolution of reaction products with pore water chemistry, leaching was performed on cured samples. This highlighted a very important point regarding the chemical composition of reaction products. The fact that in an acidic and basic environment (low and high pH), clay alumina was more liable to dissolution and dominant in the pore water chemistry. Therefore, it was rational to suggest that in lime and phosphoric acid treated samples, aluminate hydrate compounds were more likely to be formed. Also it was found that in lime treated Green Bentonite and Laterite Clay samples, the 2:1 layer structure of montmorillonite mineral and the coating action of free oxides on the surface of soil particles imposed inhibitive effects on the dissolution of clay alumina, respectively. Furthermore, it was found that the action of stabilizers was mainly surface associated and that they were unable to penetrate deeply through the crystalline clay structure. Finally, from engineering point of view, in comparison to acid stabilization, the lime treated samples exhibited much higher strength gains for all curing periods. Nevertheless, for Laterite Clay design mixes, the acid treated samples showed the most promising results with an almost threefold increase in the compressive strength of the natural soil over an 8 months curing period. The latter indicated that phosphoric acid can be used in a wisely manner as an alternative to alkaline stabilizers for treating acidic lateritic soils without having to remove the weak soil and replacing it with a superior material.

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ABSTRAK

Tanah liat yang mempunyai ciri kejuruteraan yang lemah boleh diubahsuai melalui penstabilan kimia yang akan menghasilkan bahan yang sesuai untuk tujuan pembinaan. Kesan penstabilan berasas kalsium keatas sifat-sifat geoteknikal telah dilapurkan oleh ramai penyelidik. Walaubagaimana pun jumlah bahan rujukan bagi mikrostruktur, molekul dan ciri-ciri pengurasan kapur serta penstabilan tanah dengan asid fosforik adalah terhad. Dalam tesis ini dua jenis tanah dari jenis galian montmorilonit dan kaolinit (i.e, Bentonit Hijau dan Kaolin Putih) dan dua tanah tropika (Tanah Liat Laterit dan Tanah Pink) telah dipilih. Objektif utama dalam penyiasatan ini adalah untuk memperjelaskan mekanisma bagaimana tanah yang berlainan jenis samada dalam keadaan berasid atau dalam keadaan persekitaran biasa dapat diubahsuaikan. Ini dapat dicapai dengan mengkaji perubahan yang terbentuk dalam matrik tanah –penstabil menggunakan Difrektometri Sinar-X (XRD), Spektrometri Sinar-X Serakan Tenaga (EDAX), Mikroskopi Imbasan Elektron Pancaran Medan (FESEM), Spektroskopi Infra Merah Fourier Jelmaan (FTIR), Spektroskopi Salunan Magnetik Nuklear (NMR), Kapasiti Penukaran Kation (CEC) dan analisis luas permukaan, (BET). Untuk mengaitkan perkembangan struktur yang terhasil dengan bahan kimia air liang, ujian pengurasan dijalankam ke atas sampel tanah yang diawet. Ini dapat menerangkan dengan lebih jelas komposisi kimia bahan yang terhasil daripada tindakbalas. Adalah menjadi kenyataan bahawa dalam persekitaran samada berasid atau persekitaran biasa (pH rendah dan tinggi), alumina dalam tanah liat lebih bersedia untuk dileraikan dan ketara dalam air liang. Dengan itu adalah wajar untuk menyatakan bahawa dalam penstabilan tanah dengan kapur dan asid fosforik, sebatian aluminat hidrat adalah bahan yang akan terbentuk. Didapati juga dalam penstabilan kapur keatas tanah Bentonit Hijau dan Tanah Liat Laterit, lapisan struktur 2:1 mineral montmorilonit dan tindakan salutan oksida bebas keatas permukaan zarah tanah menyebabkan terhalangnya proses peleraian alumina tanah liat. Adalah juga didapati tindakan penstabilan adalah hanya pada permukaan dan tidak dapat menembusi kedalam struktur tanah terhablur. Akhir sekali daripada sudut kejuruteraan, dibandingkan dengan penstabilan asid, penstabilan kapur menunjukan peningkatan kekuatan tanah yang lebih ketara bagi semua masa awetan. Walaubagaimanapun bagi semua rekabentuk campuran Tanah Liat Laterit, penstabilan asid menunjukan lebih keupayaan dengan mencapai 3 kali ganda kenaikan dalam kekuatan mampatan keatas tanah yang tak distabilkan bagi jangka masa awetan selepas 8 bulan. Ini menunjukan bahawa asid fosforik boleh digunakan secara terkawal seabagai bahan altenatif kepada penstabilan alkali bagi tanah laterit berasid tanpa perlu membuang tanah tersebut dan digantikan dengan tanah yang lebih baik.

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS	-	Atomic adsorption spectrophotometer
ADU	-	Acquisition data unit
AEC	-	Anion exchange capacity
Al	-	Aluminum
Al^{3+}	-	Aluminum cation
$Al(OH)_3$	-	Aluminum hydroxide
Al_2O_3	-	Aluminium Oxide
APH	-	Aluminate phosphate hydrate
$AlPO_4$	-	Aluminum phosphate
ASTM	-	American society of testing material
AT	-	Acid treated
Ba	-	Barium
Ba^{2+}	-	Barium cation
$BaCl_2$	-	Barium Chloride
BET	-	Brunauer emmett and teller
BS	-	British standard
c	-	constant
Ca	-	Calcium
Ca^{2+}	-	Calcium cation

$CaCO_3$	-	Calcium carbonate
CAH	-	Calcium aluminate hydrate
CaO	-	Calcium oxide
$Ca(OH)_2$	-	Calcium hydroxide
CASH	-	Calcium aluminate silicate hydrate
$CaSO_4$	-	Calcium sulphate
CEC	-	Cation exchange capacity
Cl	-	Chloride
CSH	-	Calcium silicate hydrate
C_s	-	Concentration adsorbed on soil surfaces
C_e	-	Concentration in water
CO_2	-	Carbon dioxide
cps	-	counts per second
Cu	-	Copper
d	-	distance of interplanar spacing as function of θ
D	-	Dielectric constant of medium
DTA	-	Differential thermal analysis
DTG	-	Derivative thermal gravimetric
e	-	electronic charge
EDAX	-	Energy dispersive x-ray analysis
EE	-	Equilibrium extraction
F	-	Fluoride
Fe	-	Iron
Fe^{2+}	-	Iron (II) cation
Fe^{3+}	-	Iron (III) cation

Fe_2O_3	-	Ferric Oxide
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
GB	-	Green Bentonite
gr	-	grams
H	-	Hydrogen
H^+	-	Hydrogen cation
HCL	-	Hydrochoric acid
H_2O	-	Water
H_3PO_4	-	Phosphoric acid
H_3PO_3	-	Phosphorous acid
HPO_3^{2-}	-	Phosphonate ion
hr	-	hours
ICL	-	Initial consumption of lime
ICP	-	Inductively coupled plasma
K	-	Potassium
K^+	-	Potassium cation
k	-	Boltzmann constant
KBr	-	Potassium bromide
Kg	-	Kilograms
k_{des}	-	desorption rate
k_{ads}	-	adsorption rate
kPa	-	kilo Pascal
LC	-	Laterite Clay
LL	-	Liquid limit

LOI	-	Loss on ignition
LT	-	Lime treated
LVDT	-	Linear variable displacement transducer
MAS	-	Magic angle spinning
MDD	-	Maximum dry density
mEq	-	milliequivalents
Mg	-	Magnesium
MgO	-	Magnesium oxide
MM	-	Mercury microporosimetry
M	-	Months
n	-	order of diffraction
n_0	-	electrolyte concentration
Na	-	Sodium
Na^+	-	Sodium cation
Na_2O	-	Sodium oxide
NH_4^+	-	Ammonium ion
N_m	-	Number of molecules
NMR	-	Nuclear magnetic resonance
NO_3	-	Nitrate
O	-	Oxygen
OC	-	Organic content
$(OH)^-$	-	Hydroxide ion
OMC	-	Optimum moisture content
P	-	Phosphorous
Pb	-	Lead

PI	-	Plasticity index
PL	-	Plastic limit
P_2O_5	-	Phosphorus oxide
PO_4^{3-}	-	Phosphate ion
ppm	-	parts per million
PS	-	Pink Soil
Pt	-	Platinum
S	-	Sulfur
sec	-	seconds
SEM	-	Scanning electron microscope
Si	-	Silicon
SiO_2	-	Silica
SO_4	-	Sulfate
SSA	-	Specific surface area
T	-	Temperature
TEM	-	Transmission electron microscopy
TG	-	Thermal gravimetric
TGA	-	Thermal gravimetric analysis
UCS	-	Unconfined compressive strength
UT	-	Untreated
ν	-	volume of gas adsorbed per unit weight of clay at a pressure
ν_m	-	volume of gas adsorbed for monolayer coverage
WK	-	White Kaolin
XRD	-	X-ray diffraction

XRF	-	X-ray fluorescene
Zn	-	Zinc
1/k	-	the effective thickness of the diffuse layer
v	-	cation valence
ε_0	-	permittivity of vacuum
ε	-	Strain
μ	-	Micro
λ	-	Wave-length
θ	-	critical angle of incidence of the x-ray beam on the crystal plane

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CHAPTER 1

INTRODUCTION

1.1 Importance of Soil Stabilization

In general soil stabilization is regarded as any process such as chemical, thermal, mechanical by which some undesirable properties of soil are mitigated or overcome (Ingles, 1972). In engineering practice, the chief properties of a soil which may require improvement are strength, permeability, and durability. The most widely recognized form of stabilization is compaction, which improves the mechanical stability of virtually any soil. However compaction alone is often seems to be insufficient in improving the behavior of fine-grained soils. Therefore the stabilization of clayey soils by incorporation of chemical additives such as lime is a technique widely used throughout the world. In fact the addition of admixtures to soils to upgrade and enhance their use in construction has a very long history. For instance, the foundation of a sixteenth century bridge in North Eastern of Iran was built using compacted mixtures of clay and lime (Bell, 1988).

During the past few decades, due to the fast growing economy there has been an increasing demand in road transportations. This has forced governments to build more roads and interstate highways. On the other hand, the presence of weak clay deposits at various sites and the need for their replacement with a superior material has imposed great costs on the construction projects. In such problematic soils, chemical stabilization techniques have proven to be effective. On the other hand,

although this technique has shown good results in numerous applications such as the construction of the Fort Worth airport in Dallas which is one of the largest clay improvement projects ever attempted (Thompson, 1972), however, in some occasions when efforts are made to stabilize the soil, the improper use of chemical stabilizers have led to millions of dollars of damage, as discussed by Wiggins *et al*. (1978). Hence, as a geotechnical engineer we need to develop our knowledge of stabilization techniques in dealing with soft soil deposits.

1.2 Chemical Stabilizers

Due to an extensive variability in particle size, mineral type, and impurities encountered in natural soil deposits, it is usually difficult to find a single stabilization technique suitable for improving soil properties.

In general, the more common stabilization techniques involve calcium based stabilizers such as lime or cement. The combination of medium pH which provides the natural pozzolans (clay silica and clay alumina) required for the pozzolanic reactions renders an enhanced material with substantial benefits. However, in some cases involving soils with high sulfate contents, treatment with conventional calcium-rich additives has led to excessive swelling and heaving (Hunter, 1988; Mitchell and Dermatas, 1992; Kota *et al*., 1996; Rollings *et al*., 1999). Therefore, liquid stabilizers that do not contain calcium can be used in sulfate-rich soils without causing excessive expansion due to this phenomenon. In addition, being cheaper to transport than traditional bulk stabilizer materials makes these products a potentially attractive alternative.

Many different liquid stabilizers are currently being used in road stabilization projects. According to Rauch *et al*. (2003) these additives can be classified into three main categories, i.e., ionic, enzyme, and polymer stabilizers. Usually they are diluted in water and sprayed onto the soil to be treated prior to compaction. These stabilizers are believed to work through a variety of mechanisms including encapsulation of

clay minerals, exchange of interlayer cations, breakdown of clay mineral with expulsion of water from the double layer, or interlayer expansion with subsequent moisture entrapment (Scholen, 1992; Petry and Das, 2001).

1.3 Importance of Research

Tropical lateritic clays with high moisture content are regional soils in Malaysia. These soils mostly occur at hillside and therefore provide excellent borrow areas for extensive use in various construction activities. However, their optimum use has been limited by a number of difficulties in construction related to their workability, field compaction and strength. Furthermore, in East and West Malaysian Peninsular, for instance along the West coast at Johor and Malacca, there are extensive number of soft kaolin deposits ranging from 5m to 20m in thickness. These deposits are formed under tropical weathering conditions in areas where precipitation is relatively high, and there is good drainage to ensure leaching of cations and iron from acidic granitic rocks (Mitchell and Soga, 2005).

As was stated before, in lime stabilization, the clay minerals are considered to be the primary source of silica and alumina required for the pozzolanic reactions. The supplies of lime in the form of hydrated lime are relatively high in Malaysia, making lime an economically viable option for the treatment of tropical soils. However, in these regions due to the high amount of iron and aluminum oxides present in the soil environment (e.g., lateritic soils), the effectiveness of lime treatment technique has been difficult to predict. Furthermore, the acidic nature of tropical soils (e.g., kaolin soils) dictated by extreme weathering conditions have raised doubts about the chemical nature of soil-lime reactions in a low pH environment and hence their longer term improvement.

In recent years, depending on the nature and function of the soil, many different chemical stabilizers have been proposed to stabilize the soil. However the use of acidic additives such as phosphoric acid has been limited. In comparison to

lime treatment, phosphoric acid stabilization is a potentially attractive alternative for treating lateritic soils (Lyons and McEwan, 1962; Sutton and McAlexander, 1987; Medina and Guida, 1995). This is because phosphoric acid reacts with free iron and aluminum oxides present in the soil environment producing hard cementitious compounds that can bind the soil particles together (Winterkorn, 1962). On the other hand, implementation of phosphoric acid as a soil stabilizer in an actual field project requires standard laboratory test on natural and acid treated samples, prepared under controlled conditions, which can be used to predict its potential effectiveness in modifying the engineering properties of the soil.

In this thesis an attempt was made to identify the underlying mechanisms that contribute to the stabilization process of phosphoric acid and lime treated clayey soils. More specifically, attempts have been made to evaluate which constituents or family of constituents present in the soil play the major role in this phenomenon. For fulfillment of this goal, the changes in micro-structural, molecular, and leaching characteristics of the treated soil were monitored using various microscopic and spectroscopic techniques. For instance, in the micro-structural characterization, the time-dependent changes in the properties of the treated soil were studied at the particle level. In addition to evaluate the relative success of phosphoric acid in comparison to the alkaline stabilizer (lime), unconfined compressive strength test as an index of soil improvement was performed on cured samples.

1.4 Aims and Objectives

Based on the literatures published in the field of soil stabilization, there are two main reactions responsible for the soil enhancement due to chemical treatment:

a) Ion-exchange reactions

b) Dissolution of clay structure and formation of reaction products

The short-term process involving ion-exchange reactions are well understood, although they have not been fully studied in the context of acid stabilization. On the other hand, the long-term mechanism which consists of soil-stabilizer interaction and the formation of new cementitious compounds are poorly understood, particularly in the case of phosphoric acid treatment. Also little research has been carried out to determine how different clay minerals respond to various pH environments.

The main aim of this thesis was to identify and assess the different processes involved in soil-stabilizer interaction under acidic and basic conditions. Therefore by utilizing the various test procedures described by previous researchers with appropriate adjustments in some cases, the micro-structural, molecular, and leaching characteristics of lime and phosphoric acid stabilized soils were analyzed and compiled to obtain useful relationship between the monitored chemical reactions and the physiochemical behavior of the soil. Furthermore, the results could be used as guidelines to better understand the effect of other alkali or acidic additives on clayey soils.

Based on the structural properties and environmental conditions experienced in tropical regions, four type of soil were selected. First of all, to increase the likelihood of observing subtle soil-stabilizer reactions, the more expansive and pure Bentonite soil comprised mainly of sodium-montmorillonite mineral was used in this investigation. The Second type of soil was a white and odorless kaolin powder. It should be noted that the minerals present in these two soil types (montmorillonite and kaolinite) represent the opposite extremes of structural charge developments, hence they can serve as index for predicting the behavior of other clay minerals which exhibit intermediate behaviors. The third type was a highly weathered lateritic soil commonly found in tropical regions. Finally, a native silty clay (Pink soil) collected from Southern part of Malaysian Peninsular was used in the physiochemical characterization study.

In this thesis, at least six mix designs were prepared for each soil type. Also because it was important to compare the efficacy of the two stabilizers, similar amounts was decided to be used for some samples. The characterization tests were

performed over three curing periods. After 1 month of curing to evaluate the short term ion-exchange reactions and after 4 and 8 months of curing to assess the time-dependent changes in the physiochemical behavior of the soil-stabilizer matrix and moreover to monitor the evolution of reaction products. It should be stressed that, due to the high quantity of the samples and also the high cost of modern analyzing techniques such as Nuclear Magnetic Resonance (NMR) spectroscopy, an attempt was made to perform most of the chemical tests using the available resources within the UTM laboratories. In addition, some of the tests were limited to the reference samples which showed the highest degree of improvement.

Finally, fulfillment of this aim was achieved by meeting the following objectives:

a) Index the formation and hardening of reaction products using unconfined compressive strength test.

b) Observe the time-dependent changes in the cation exchange capacity (CEC), pH, and surface area value of the treated soil.

c) Monitor the mineralogy and elemental composition of the treated samples by determining the micro-structural characteristics of soil-stabilizer matrix at different time intervals.

d) Observe the morphological changes on the surface of soil particles from the short-term to the long-term in order to identify the new formed amorphous and crystalline compounds.

e) Assess the changes induced on the molecular structure and local bonding of clay particles in an attempt to study the magnitude of stabilizer penetration into the crystalline clay structure and its interlayers.

f) Investigate the effect of chemical stabilizers on the dissolution of clay structure in order to correlate the structural evolution of reaction products with pore water chemistry via performing leaching test on cured samples.

g) Finally based on the data collected from various spectroscopic and microscopic techniques, the more realistic soil-stabilizer interactions has been proposed and discussed. Also apart from clarifying the underlying mechanisms, a comparison between the efficacy of acidic and basic stabilizers were made.

1.5 The Thesis

This thesis aims to investigate the physiochemical behavior of lime and phosphoric acid stabilized clayey soils.

In this chapter the importance of chemical stabilization in soil improvement and the necessity to understand the mechanisms associated with this process was concisely discussed. In addition the research philosophy divided into two main categories, i.e., ‘importance of research’ and ‘aims and objectives’ were also presented.

In chapter 2, the fundamentals of clay mineralogy are presented. This was considered essential in order to better understand and elucidate the more sophisticated soil-chemical reactions. Different chemical stabilization techniques were reviewed thereafter followed by the hypothesized mechanisms suggested on the formation of reaction products. Finally based on the current scientific knowledge on soil stabilization a research framework was obtained.

Chapter 3 describes the comprehensive chemical analysis and methods used to study the time-dependent changes induced on the structure of treated soils. The laboratory experiments performed for determining the geotechnical properties of the soil followed the procedures described in the British Standard (BS). Furthermore, micro-structural, molecular, and leaching characterization of the soil using various spectroscopic and microscopic techniques were carried out based on the published

papers and standards available. The results obtained from these tests are presented and discussed in detail in chapter 4.

Finally, chapter 5 concludes the outcome of this study and highlights areas where further research can be carried out.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

With the reduction of available land resources, more and more construction of civil engineering structures is carried out over soft soil deposits which are commonly found in many parts of the world. The behavior of these deposits is strongly influenced by the mineralogical composition and environmental conditions. Furthermore, because of their high compressibility and low shear strength they impose severe engineering problems. In such problematic soils, chemical stabilization techniques have proven to be effective. Improved strength and workability are just some of the beneficial effects of soil treatment. This review aims to:

a) Introduce various types of non-traditional additives currently available in the market.

b) Outline the more important characteristics of clay particles such as mineral structure and ion-water interaction in order to better understand how the chemical properties of clayey soils can affect the soil-stabilizer reactions.

c) Present the recent findings on lime and phosphoric acid stabilization and the results obtained regarding their application in different soil types.

d) Describe few of the analytical techniques that can be used to study the stabilization process more effectively.

2.2 Non-Traditional Stabilizers

Engineers, architects, and contractors have tried many ways to reduce the damaging effects of soft clays. Their actions were often based on trial-and-error approaches. They have used mechanical stabilization to the extent practical but have found it also necessary to alter the Physicochemical properties of clayey soils in order to permanently stabilize them.

A stabilizer in general can be defined as a chemical compound that has the ability to pose an immediate and long-term enhancement in the engineering properties of the soil. This is achieved by various mechanisms. Chemical stabilizers based on their common field application can be divided into two broad categories, i.e., traditional and non-traditional stabilizers. Traditional stabilizers such as lime and cement have been discussed comprehensively in numerous literatures and hence this section will mainly focus on non-traditional stabilizers.

The use of chemical agents other than lime to improve clay soils was introduced when Carroll and Starkey (1971), clay mineralogists, published their findings on reactivity of clay minerals with acids and alkalis. In recent years, there has been a proliferation of literature regarding the application of non-calcium based stabilizers for soil stabilization. For instance, the effectiveness of three liquid soil stabilizers in improving the engineering properties of clayey soils was evaluated by researchers at the University of Texas (Rauch *et al*., 2002). Based on their findings, there were no significant changes in soil properties at the recommended stabilizer application rates. Santoni *et al*. (2002), studied the wet and dry strength gain of a silty-sand material stabilized with 12 nontraditional stabilizers, including acids, enzymes, lignosulfonates, petroleum emulsions, polymers, and tree resins. They

reported a large variation in results with some stabilizers performing well and other stabilizers not performing at all for the experimental conditions and soil they used.

Currently, various liquid stabilizers are actively marketed for stabilizing soils on highway projects. These stabilizers can be classified into three main categories. That is, ionic stabilizers, which are believed to work through a ion-exchange process within the clay structure. Secondly, the enzyme stabilizer which is reported to act in several different ways, including the breakdown of clay minerals with expulsion of water from the double layer, the binding of clay particles by aggregation, and interlayer expansion with subsequent moisture entrapment (Scholen, 1992). Finally, the polymer stabilizer which with its strongly adhesive nature is alleged to coat the surface of soil particles causing them to bond together rather than chemically altering the clay inner layers.

In the following paragraphs, some of the more common non-traditional stabilizers will be discussed briefly.

a) **Acids:** Acid stabilizers have shown some promising results in acidic soil types. In particular, the use of phosphoric acid in treatment of lateritic soils with high oxide content has gained much attention. In general, the acid stabilizers increase the (H^+) ion concentration in the pore water. The (H^+) ions are then exchanged onto the clay lattice releasing (Al^{3+}) ions which subsequently reacts with anions present in the solution to form cementitious compounds. Furthermore, it may form hydroxyl aluminum ions ($Al(OH)^{2+}$) that can be held in the clay interlayers. This process reduces the cation exchange capacity (CEC), which will reduce the shrink-swell characteristics of the clay.

b) **Electrolytes (Salts):** The hydration of exchangeable cations like sodium, calcium, and magnesium is believed to be the main cause of swelling in expansive minerals such as montmorillonite. The amount of water attracted to these cations is directly proportional to the ionic-charge to ionic-radius ratio. Therefore, larger cations with a lower charge attract less water. Therefore,

addition of potassium and ammonium salts to the soil will result in less expansion of clay mineral lattice when less hydrated ions like (K^+) and (NH_4^+) replace more hydrated ions in the interlayer sites. Because the salts travel in the soil solution by diffusion, they are best applied under saturated conditions.

c) **Enzymes:** Enzymes are protein molecules which are made up of amino acids. They can speed up a biochemical reaction by orders of magnitude, but the most amazing thing is that they react with specific bonds in compounds. Some enzymes require a higher fraction of silt and clay with associated humus to provide an organic source to react with the enzymes. It is important to compact soils treated with these stabilizers prior to curing. The greater the compacted density, the more effective the stabilization will be.

d) **Polymers:** Polymers are defined as linked, simple molecules that may be natural or synthetic. Natural polymers include proteins, cellulose, and rubber. Most synthetic polymers are organic compounds such as nylon, Teflon, and Plexiglas. One may use a chain as an analogy. Each link in the chain is a simple molecule that is attached to other links (simple molecules) by strong covalent bonds. Organic polymers have been used by soil scientists to stabilize soil aggregates. They tend to be medium to heavyweight organic cations or anions that can replace other ions on clay surfaces. They may bridge soil particles and prevent water ingress, thus reducing shrink-swell.

e) **Resins:** Resins are adaptable to various climatic conditions and do not react with the soil but coat the soil particles forming a barrier to water. The cost is typically 1.5 to 4 times the conventional stabilization techniques.

f) **Sulfonated Oils:** Sulfonated oils are oils that have been chemically treated with sulfuric acid to make them soluble in water. The oils are ionized by the sulfuric acid generating a net negative charge which makes them attract cations. These stabilizers are reported to pull cations and water from the clay structure and create amorphous silica (SiO_2) and gibbsite ($Al(OH)_3$) from the tetrahedral and octahedral sheets of the clay minerals in the process.

2.3 Clay Characteristics

Among different types of soils, clay deposits are of particular interest due to their considerable variation in terms of composition and engineering properties. The definition of clays is diverse. Based on the knowledge of a geotechnical engineer, clay principally is a fine-grained inorganic material having the ability to normally demonstrate marked plasticity when wet, and in general, the properties such as adsorption, hydration, ion exchange, and hardening when exposed to different environmental conditions.

One of the major factors which influence the reactivity of a soil, i.e., the ability of a soil to react with chemical additives to produce cementitious compounds, is the clay fraction. Clay-stabilizer reactions are complex and not completely understood at this time. Therefore, a prior knowledge of clay properties and the minerals present in a fine-grained soil provides an intuitive insight as to its behavior.

2.3.1 Clay Minerals

Clay soils have a wide range of mineralogical composition. They may consist of various proportions of different type of clay minerals, notably kaolinite, illite, and montmorillonite and of non-clay minerals, notably quartz, and/or organic matter. The crystalline clay minerals belong to the mineral family termed phyllosilicates (Greek phyllon, leaf) which is because of their leaf-like or planar structure. They are comprised of two basic building blocks, a sheet of silicate tetrahedral and the other an octahedral sheet. The tetrahedral and octahedral sheets are the fundamental structural units of these minerals. Hence different clay mineral can be formed by the stacking arrangements of sheets of these units and the manner in which two or three successive layers are held together (Figure 2.1). It should be noted that the bonds that link the unit layers together to form particles are the reason for the variable response of the clay minerals in terms of plasticity and consistency. On this basis the clay minerals are classified into two different groups; 1:1 type minerals or the kaolin

group and the 2:1 type minerals or the illites and smectite groups. The structure and detailed characterization of most common clay minerals found in soil deposits are described briefly in this section.

2.3.1.1 Kaolinite

Kaolinite mineral is the most prominent member of kaolin group. As shown schematically in Figure 2.2, kaolinite formation is favored when alumina is abundant and silica is scarce because of the 1:1 silica to alumina structure. Conditions leading to kaolinite formation usually include areas where precipitation is relatively high, and there is good drainage to ensure leaching of cations and iron. As can be seen each kaolinite particle is comprised of a series of hexagonal shape layers much like the pages of a book. These layers are bound to other adjacent layers by hydrogen bonding. Consequently, cations and water do not enter between the structural layers of kaolinite. Therefore, in contrast with other clay minerals, kaolinite exhibits less plasticity, cohesion, and swelling.

2.3.1.2 Montmorillonite

Montmorillonite is the most common mineral of smectite group. Conditions favoring formation of montmorillonite type minerals are high pH, high electrolyte content, and the abundance of silica. Also climatic conditions where there is poor leaching and drainage favor the formation of smectite. The small, very thin, and filmy particles of this mineral are shown in Figure 2.3. These layers are loosely held together by very weak bonding. Hence exchangeable cations and associated water molecules are easily attracted between the interlayer spaces, causing expansion of the crystal lattice. It should be noted that, the type of adsorbed cations exerts a controlling influence on the behavior of these minerals.

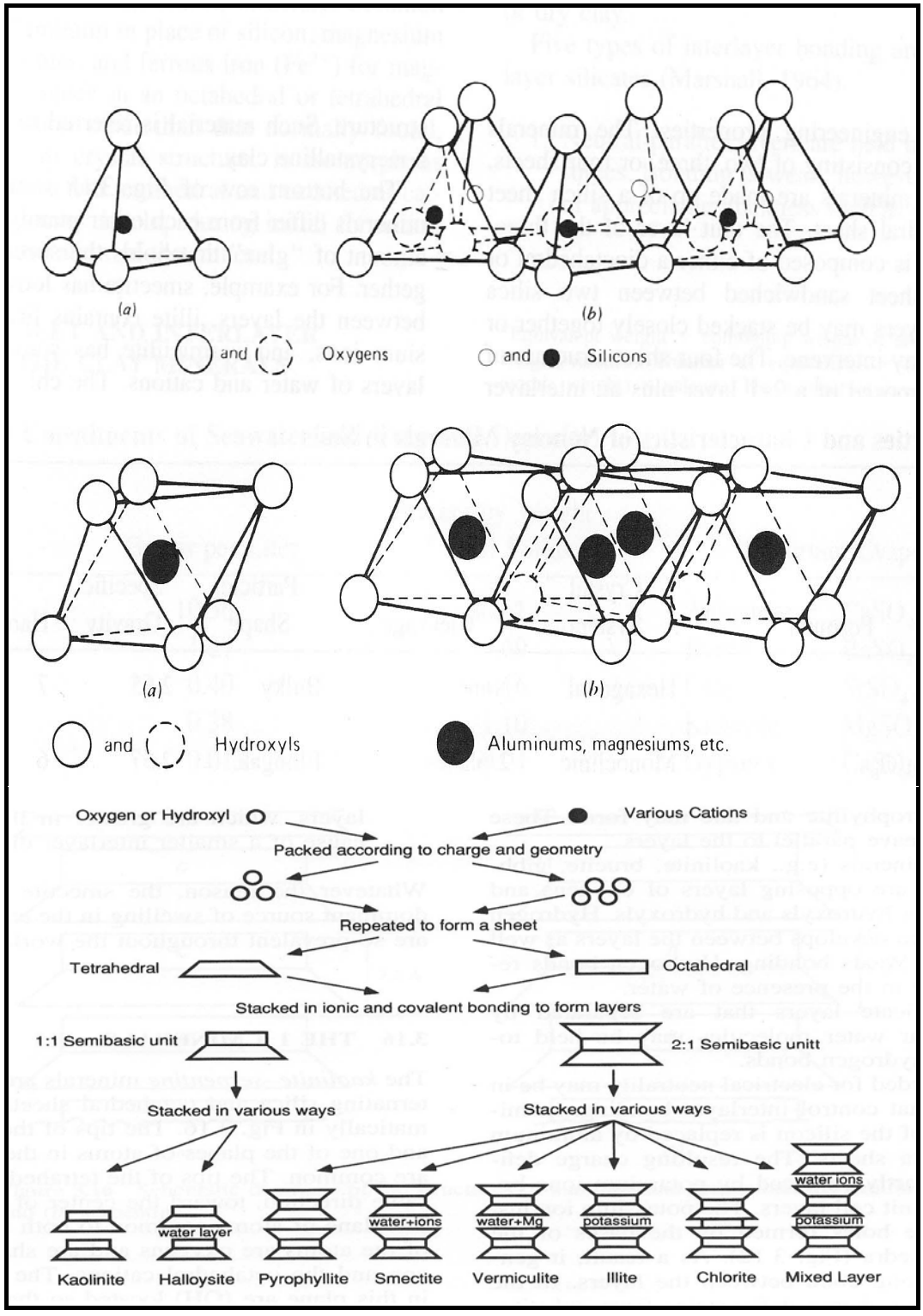


Figure 2.1 Basic sheet arrangements of silica tetrahedral and aluminum octahedral and synthesis pattern of clay minerals (Mitchell and Soga, 2005)

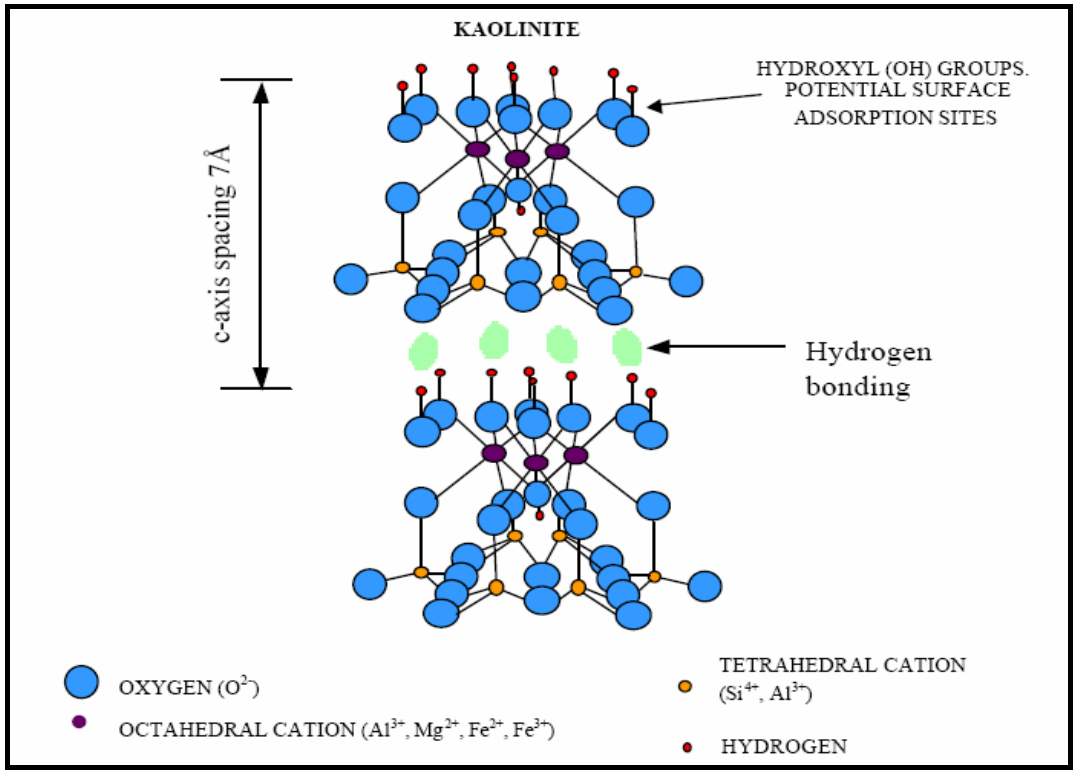
2.3.1.3 Illite

Illite is one of the most common clay minerals found in soil deposits encountered in engineering practice. They form under conditions similar to those leading to the formation of smectites. In addition, the presence of potassium is essential. The high stability of illite is responsible for its abundance and persistence in soils and sediments. The crystal layers of these mineral are characterized by an octahedral sheet sandwiched between two tetrahedral sheets. As can be seen in Figure 2.4, non-exchangeable potassium ions are strongly attracted in the interlayer space, acting as a binding agent, preventing expansion of the crystal. Therefore, illite minerals are quite non- expansive. The morphology of these particles is often flaky and thin at the edges.

2.3.2 Clays from Tropical Regions

The physical and chemical nature of soil surface layers varies considerably from point to point and is controlled by the weathering conditions of the local environment. In general soil deposits can be considered as complex, dynamic, multi-component and multi-phasic systems.

Tropical soils have significant differences from the more common soils of temperate climates. In these regions, rock weathering is intensive and is characterized by the rapid breakdown of feldspars and ferromagnesian minerals, the leaching of silica and the deposition of Fe_2O_3 and Al_2O_3 (Mitchell and Soga, 2005). This process is termed laterization (Gidigasu, 1972). Laterite as a soil group, rather than a well-defined material, is found in these humid tropics where heavy rainfall and warm temperatures under good drainage conditions leads to the formation of thick horizons of lateritic soil profiles comprised mainly of free oxides and kaolinite minerals (Townsend, 1985). However, as weathering proceeds, the kaolinite content decreases, and the hydrated iron and aluminum oxides progressively alter to hematite (Fe_2O_3). Because of the high iron concentration, the resulting soils are usually red.



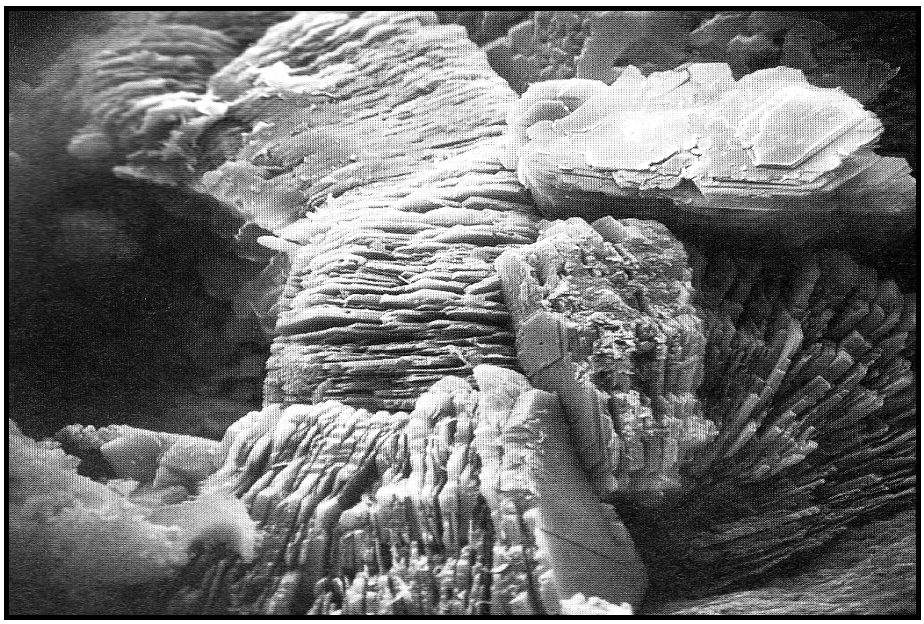
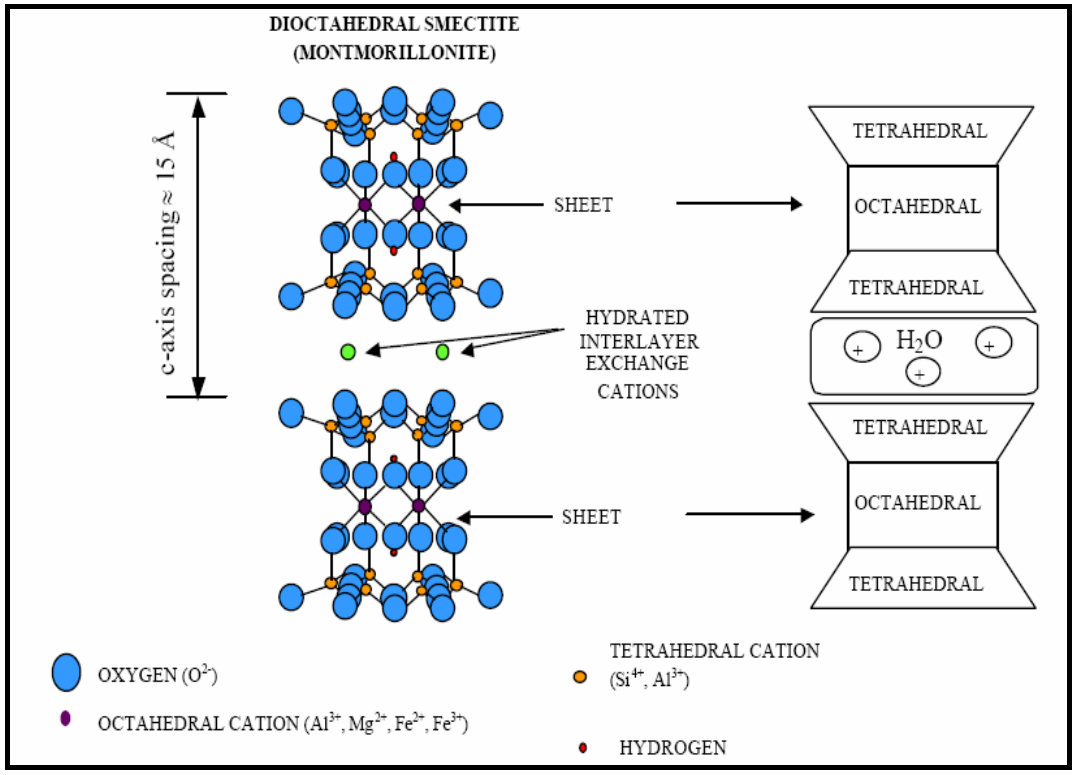


Figure 2.2 Structure and morphology of kaolinite (Mitchell and Soga, 2005; McBride, 1994)



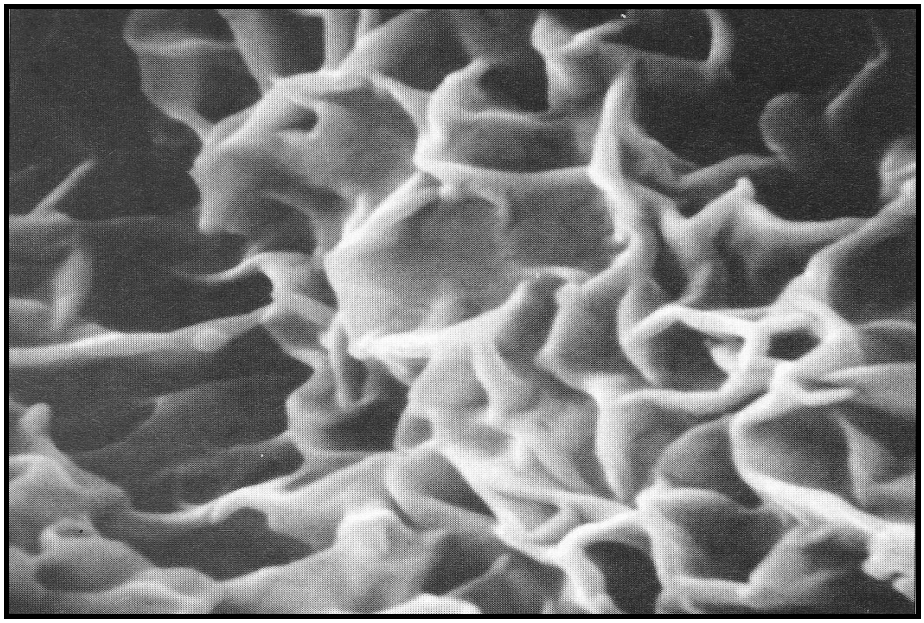


Figure 2.3 Structure and morphology of montmorillonite (Mitchell and Soga, 2005; McBride, 1994)

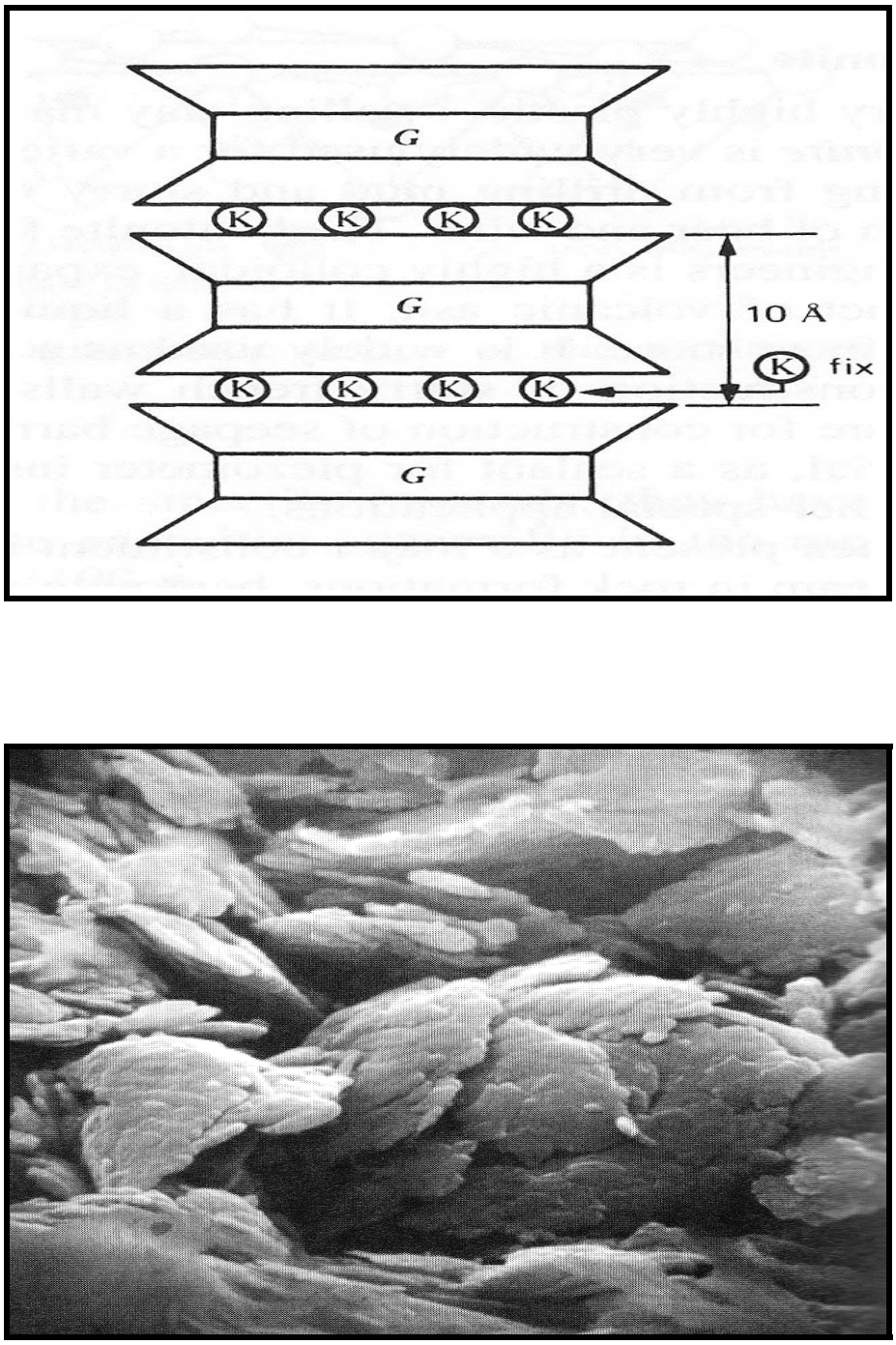


Figure 2.4 Structure and morphology of illite (Mitchell and Soga, 2005; McBride, 1994)

2.3.3 Clay-Water Interaction

Clay particles due to their very small size, unique crystal structure, and platy shape morphology have great affinity to adsorb cations and polar liquids such as water. The nature and consequences of these interactions are quite complex. According to Mitchell and Soga (2005), several possible mechanisms for water adsorption have been proposed. They are shown schematically in Figure 2.5. As can be seen, at relatively low moisture contents, adsorbed cations are tightly held on the surface in order to neutralize the negatively charged clay particles and those in excess are present as salt precipitates. On the other hand, at higher water contents, these precipitates can go into solution. Also the adsorbed cations, because of their high concentration near the clay surface, try to diffuse away in order to equalize concentration throughout the pore fluid. Hence, as shown in Figure 2.6, the net result of a negative charged surface, as is the case with clay minerals, coupled with unfriendly cations which have a tendency to escape is a highly diffused water layer surrounding the clay particles, known as diffuse double layer. During the past decades, several theories have been proposed to quantify this layer. The theory developed by Gouy and Chapman based on one dimensional clay surface which is a reasonable assumption for platy clay particles is shown in the equation.

$$(1/k) = [(\varepsilon_0 DkT) / (2n_0 e^2 v^2)] \qquad (2.1)$$

According to this relation the effective thickness of the diffuse layer (1/k) is a function of dielectric constant of medium (D), temperature (T), electrolyte concentration (n_0), cation valence (v) , and constants ε_0 (permittivity of vacuum), k (Boltzmann constant) and e (electronic charge). It is evident that, the thickness varies inversely with the valence and the square root of concentration. This indicates that even relatively small amounts of divalent or trivalent cations added to a clay-water system, have a considerable affect on the diffuse layer thickness and thus the engineering properties of clayey soils. For instance, as can be seen in Figure 2.7, when clay particles are fully hydrated, these diffused water layers force the clay platelets into a parallel arrangement which offers very little shear strength.

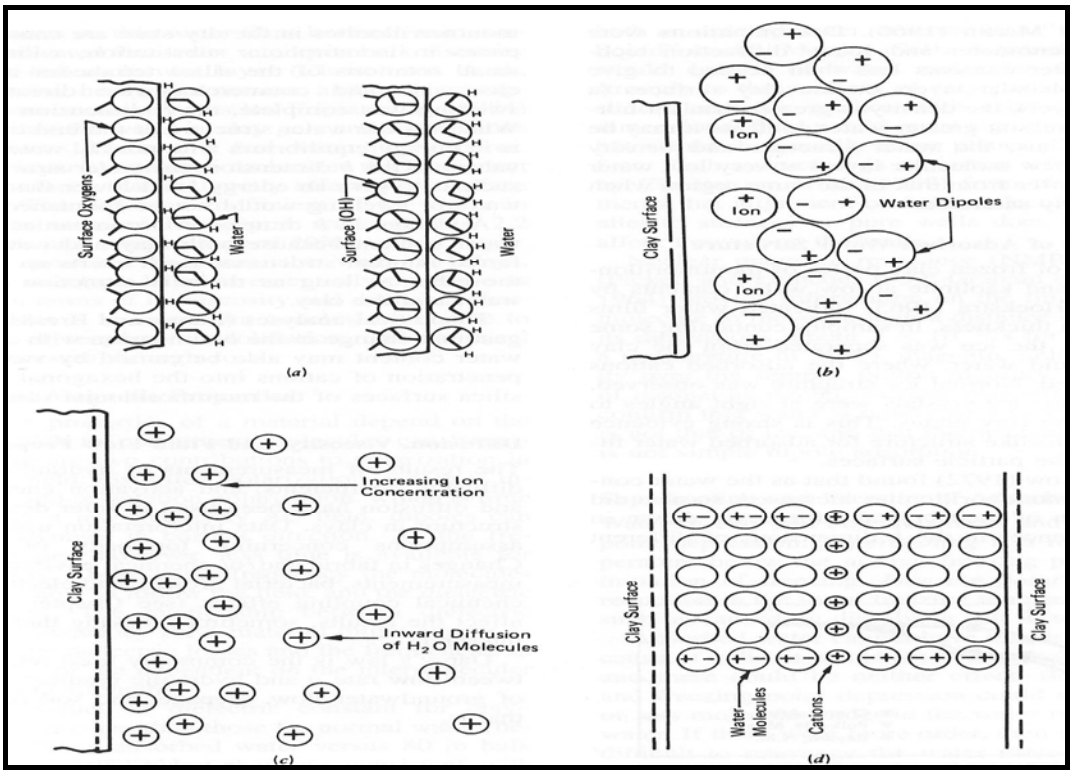


Figure 2.5 Some possible mechanisms of water adsorption by clay surfaces: (a) hydrogen bonding, (b) ion hydration, (c) attraction by osmosis, and (d) dipole attraction (Mitchell and Soga, 2005)

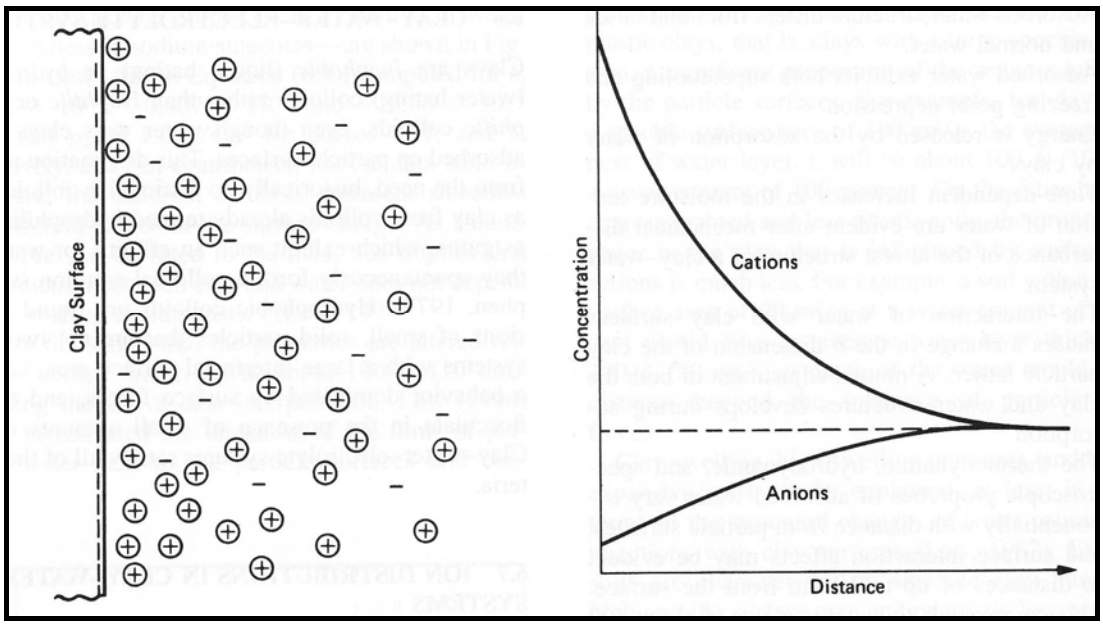


Figure 2.6 Distribution of ions adjacent to a clay surface according to the concept of the diffuse double layer (Mitchell and Soga, 2005)

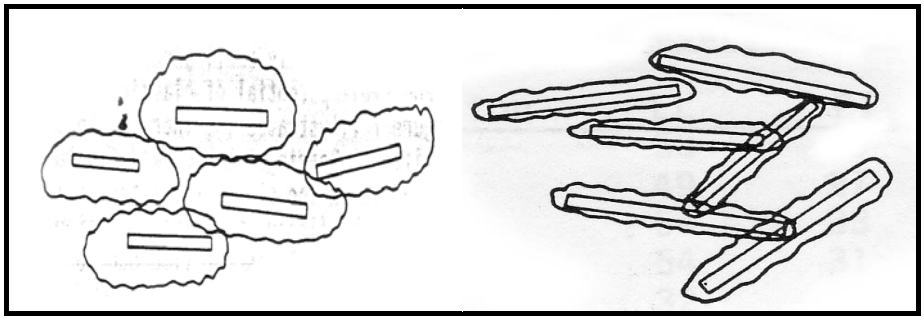


Figure 2.7 Textural modification due to the changes in the thickness of diffuse double layer (Little, 1995)

2.3.4 Cation Exchange Reactions

Under a given set of environmental conditions (temperature, pressure, pH, and chemical composition of water), clay minerals can adsorb cations of specific types and amounts. This is a surface phenomenon and usually occurs in response to the electric charge carried by the clay particles.

In general, there are two major sources of charges on clay lattice:

a) The pH-dependent charges that is associated primarily with the hydroxyl groups attached to silicon and aluminum on the surfaces and edges of the clay minerals (Mathew *et al*., 1997a). This is believed to be the major source of charge in kaolinite minerals. In kaolinite, the proton is presented as OH groups on the surface planes of the mineral. Hence, if the clay mineral is exposed to a high pH environment, the hydrogen dissociates from the OH group, leading to a negative charge on the clay surface. Exposed hydroxyl groups are also present in the sesquioxides, amorphous, and para-crystalline clays.

b) The negative charges induced by the isomorphic substitution of ions within the clay lattice. These charges are permanent feature of the mineral crystal

and do not depend upon the chemical composition of the ambient solution. For instance, the OH groups in the smectite clays are not present as exposed OH groups. They are contained within the crystal, covered by layers of silica tetrahedrons. Therefore, smectite has its negative charge mainly from isomorphous substitution.

The negative charges are usually neutralized by a swarm of positively charged ions (cations). These cations, which are held electrostatically on the surface of the soil colloids, are called adsorbed cations. Adsorbed cations can be replaced or exchanged by other cations from the soil solution. The process of replacement is known as cation exchange, and the ions involved in the exchange reaction are called exchangeable cations. This base exchange is documented by the Lyotropic series which generally states that, higher valence cations replace those of a lower valence and ordinarily smaller cations tend to displace larger cations. The Lyotropic series is written as:

$$Li^{+} < Na^{+} < H^{+} < K^{+} < NH_4^{+} << Mg^{++} < Ca^{++} << Al^{+++} \qquad (2.2)$$

The rate of ion exchange depends on clay type, solution concentration, and temperature. In general, exchange reactions in kaolinite minerals is almost instantaneous, while in expansive minerals such as montmorillonite due to the fact that, the major part of exchange takes place in the interlayer region, a longer time for complete exchange is required.

The cation exchange capacity, frequently abbreviated as CEC, is a quantitative measure of all the cations adsorbed on the surface of the soil colloids. The amount is usually expressed in milliequivalents (mEq) per 100g of soils. Because of differences in concepts, and in view of the presence of permanent and variable charges contributing to cation exchange reactions, several types of CEC have currently been identified.

The most important of these types are:

a) CEC_p, which is the CEC produced by the permanent negative charges of the clay minerals.

b) CEC_v, which is the CEC resulting from the pH dependent (or variable) charges of the inorganic and organic colloids.

c) CEC_t, which is the total CEC caused by both the permanent and variable charges of the soil colloids.

Figure 2.8 shows the relative contributions of variable pH-dependent charge sites (CEC_v) and permanent cation exchange capacity (CEC_p) to the total cation exchange capacity (CEC_t) of the soil. Depending on mineralogy, temperate mineral soils are likely to have measurable CEC_t at any pH due to the presence of CEC_p on 2:1 clay minerals, with additional CEC_v determined primarily by the amount of soil organic matter present. In addition, the presence of hydrous oxides of Fe and Al in highly weathered tropical soils may result in a net positive charge and the dominance of anion exchange in these soils at low pH environment (Ross, 1989). In Table 2.1 typical cation exchange capacity values for various clay minerals are shown. As can be seen, due to the structure of the minerals, kaolinite has a very low exchange capacity, illite has a low capacity due to the very stable presence of K^+, and montmorillonite has a very high exchange capacity.

Table 2.1 : Cation exchange capacity of clay minerals (Grim, 1968)

Mineral	**Cation Exchange Capacity (meq/100 g)**
Kaolinite	3-15
Halloysite	5-50
Illite	10-40
Montmorillonite	60-150
Chlorite	10-40

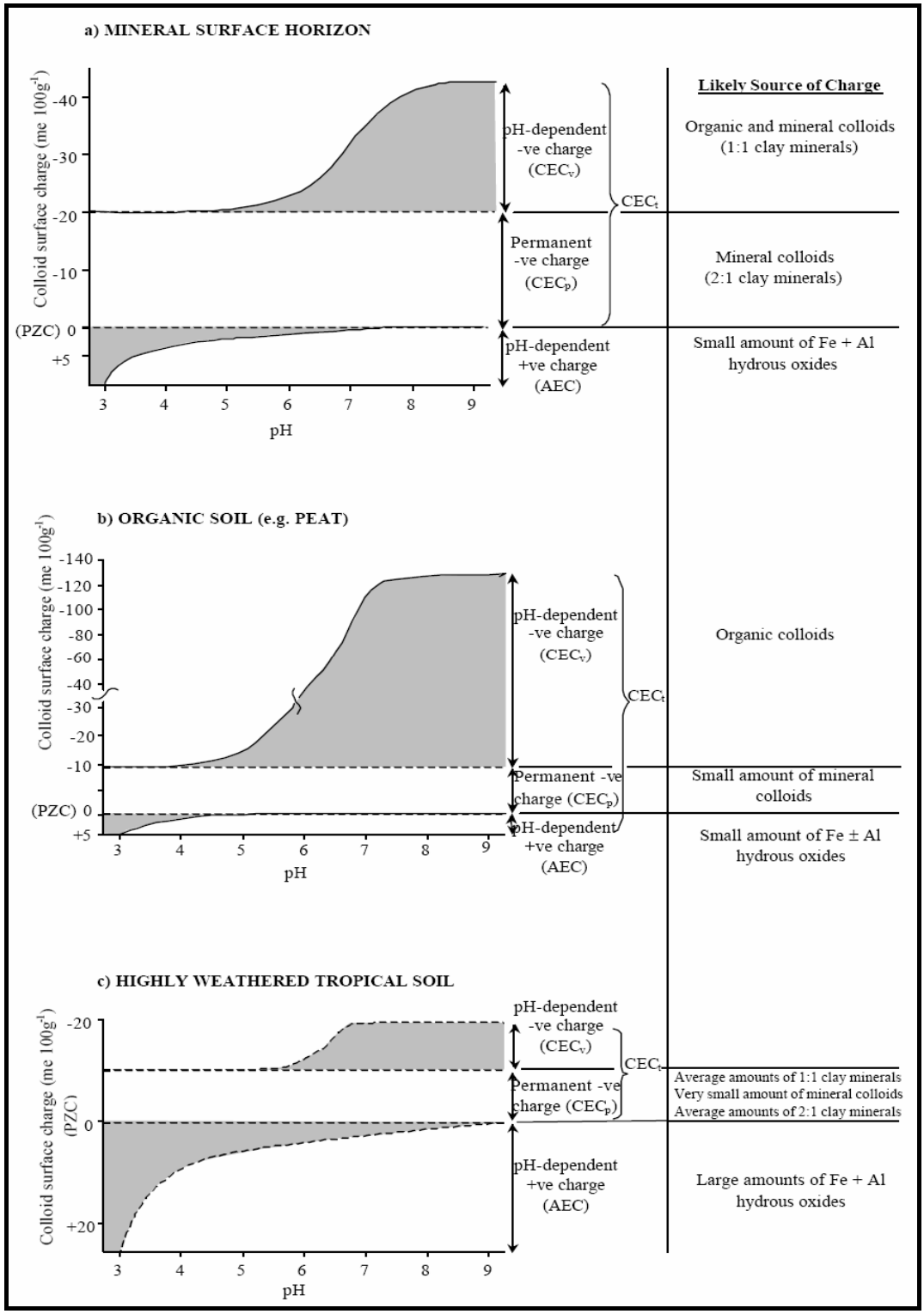


Figure 2.8 Schematic effect of pH on surface colloidal charge for temperate mineral and organic soils and tropical soils (Ross, 1989)

2.3.5 Anion Exchange Reactions

The basic principles of anion exchange are similar to those of cation exchang, except that the charges on the clay particles are positive and the exchange is among negatively charged anions. In Table 2.2, typical anion exchange capacity values for various clay minerals are shown. Also as illustrated in Figure 2.9, in contrast to cation exchange capacity, the anion exchange capacity of soils generally decreases with increasing pH value. In addition as noted by Mitchell and Soga (2005), the octahedral face of 1:1 minerals such as kaolinite and the OH termination sites on the edges of both 1:1 and 2:1 type clay minerals are affected by the pH of surrounding solution. For instance, alumina, which is exposed at the edges of clay particles is amphoteric and ionizes positively at a low pH environment. As a result positive diffuse layers can develop at the edges of some clay particles in an acidic environment promoting positive edge to negative surface interaction, leading to flocculation of soil matrix. This effect is of greatest importance in kaolinite minerals.

Table 2.2 : Anion exchange capacity of clay minerals (Grim, 1968)

Mineral	Anion Exchange Capacity (meq/100 g)
Kaolinite	7-20
Illite	4-17
Montmorillonite	20-30
Chlorite	5-20

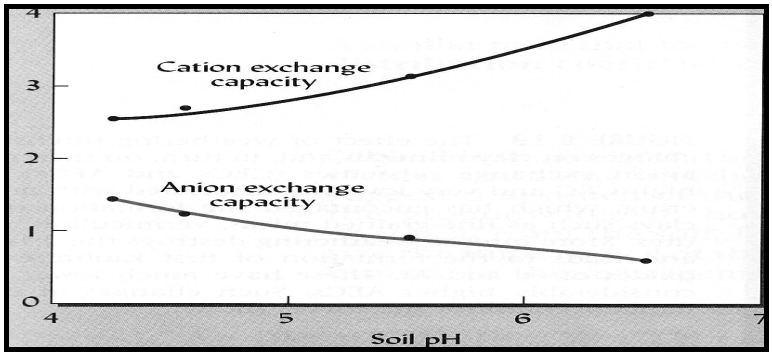


Figure 2.9 Effect of increasing soil pH on the cation and anion exchange capacities (Brady and Weil, 1996)

2.3.6 Effects of pH Value

The degree of acidity or alkalinity of an environment is a master variable that affects the chemical and physical properties of a soil (Brady and Weil, 1996). As mentioned before in pH dependent charges, the tendency for hydroxyl groups to dissociate in water is strongly affected by the pH. The higher the pH, the greater is the tendency for (H^+) to go into solution and the greater the effective negative charge of the particles would be. These (H^+) ions may be present in soils as adsorbed (H^+) ions on the surface of the colloidal complex, or as free (H^+) ions in the soil solution. The adsorbed (H^+) ions create the reserve acidity, also called the potential or exchanged acidity of soils. The free (H^+) ions are the reason for the so-called active acidity of soils. Soil pH refers to this active acidity.

In Figure 2.10, the effect of soil pH on distribution of ions is illustrated. It is apparent that there are noticeable changes in dominant cations present in the exchange complex in various pH conditions. Also as can be seen in Figure 2.11, in strongly (pH ≈ 4 to 5) and very strongly (pH ≈ 3 to 4) acid soils, Al, Fe, and Mn may exist in very high amounts because of their increased solubilities. If phosphates are present, these elements will react with the phosphates to form insoluble phosphates. Nevertheless, in highly acidic tropical soils controlling acidity is an important aspect of lime stabilization, which usually necessitates high amounts of lime to be used in order to neutralize soil acidity.

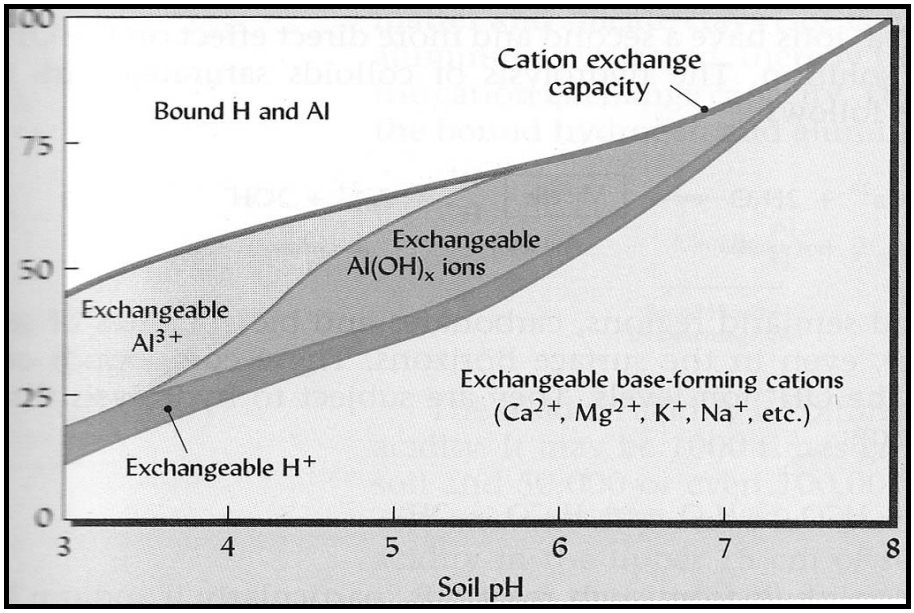


Figure 2.10 General distribution of cations held as exchangeable ions at different pH values (Brady and Weil, 1996)

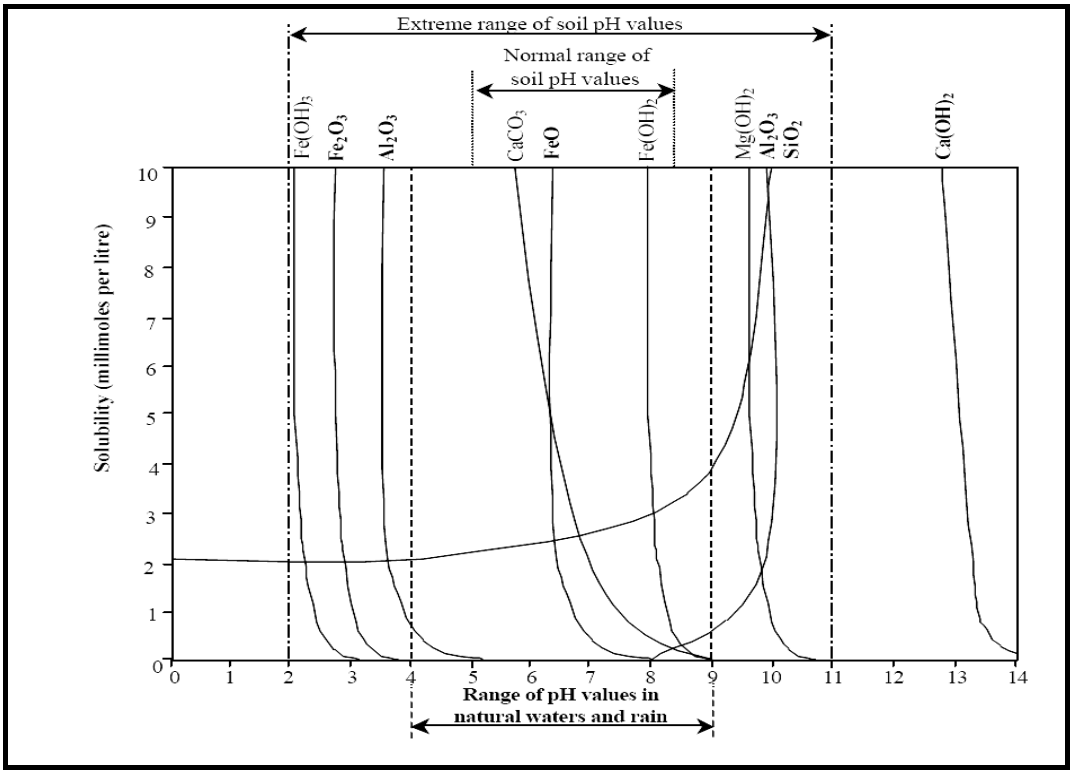


Figure 2.11 Solubility of some soil mineral species in relation to pH (Loughnan, 1969)

2.3.7 Clay-Ion Interactions

All solids terminate at a surface, or phase boundary, on the other side of which is matter of a different composition or state. In solids, atoms are bonded into a three-dimensional structure, and the termination of this structure at a surface, or phase boundary, produces unsatisfied force fields. In a fine-grained particulate material such as clay soil the surface area may be very large relative to the mass of the material and hence the influences of the surface forces on properties and behavior may be very large.

These unsatisfied forces at solid surface may be balanced in any of the following ways:

a) Attraction and adsorption of molecules from the adjacent phase.

b) Cohesion with the surface of another mass of the same substance.

c) Solid-state adjustments of the structure beneath the surface.

In most engineering materials, internal chemical and physicochemical forces of interaction bond the particles together. As shown in Figure 2.12, there are two major force fields available around clay particles. First, the double layer repulsion which similar to diffuse double layer is sensitive to changes in electrolyte concentration and cation valence and secondly, the van der Waals attraction forces which is only sensitive to changes in the dielectric constant and temperature. By combining the energies caused by these forces, the net curve of interaction can be obtained which determines the arrangement of soil particles.

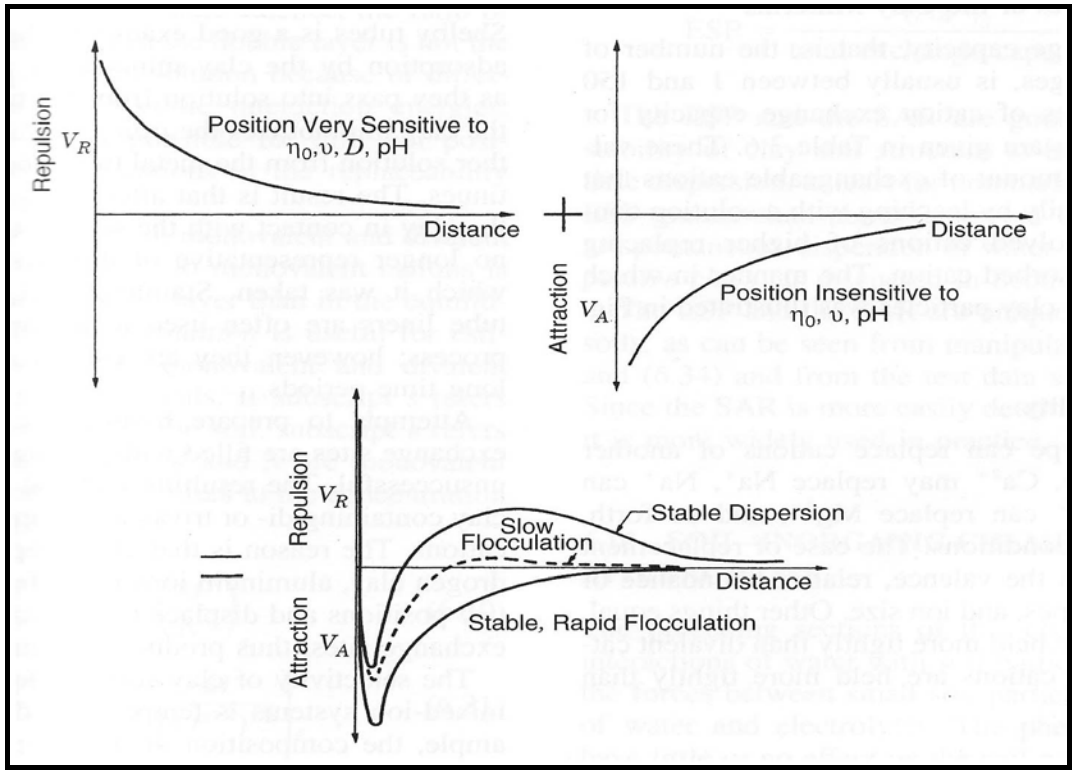


Figure 2.12 Energies of repulsion, attraction, and net curves of interaction for parallel flat plates (Mitchell and Soga, 2005)

2.3.8 Equilibrium-State Condition

Ion exchange reactions are rapid, reversible and stoichiometric, where quantities of exchanged ions are chemically equivalent. Although the exchange process can be considered instantaneous, ion diffusion to or from the colloid surface is probably the rate-limiting step, especially in heterogeneous field conditions (Bohn *et al.*, 2001). The reversible relationship between a cation in water with an exchangeable cation at equilibrium can be described by Equation 2.3 (Dragun, 1988).

$$C_s \underset{k(ads)}{\overset{k(des)}{\rightleftharpoons}} C_e \qquad (2.3)$$

Where

C_s = concentration adsorbed on soil surfaces (μg/gram soil)

C_e = concentration in water (μg/ml)

k(des) = desorption rate

k(ads) = adsorption rate

Analysis of this equation reveals that the equilibrium distribution of a cation is governed by the two opposing rate processes. The adsorption rate is the rate at which the dissolved cation in water transfers into the adsorbed state and the desorption rate is the rate at which the cation transfers from the adsorbed state into water. The adsorption coefficient K_d is the simplest way of expressing the extent of adsorption and is defined as the ratio of C_s/C_e. Hence, the more adsorption that occurs, the greater the magnitude of K_d.

Dragun (1988) stated that if ions were point charges then no preference for ions of the same valence would exist. However, ions do have significantly different hydrated sizes. Since electrostatics are involved in the attraction of ions at a charged soil surface then it can be predicted that the ion with the smallest hydrated radius and largest charge will be preferentially accumulated. As was mentioned before, this order is termed the Lyotropic series and represents increasing cation replaceability, or decreasing cation attraction, with increasing radius, increasing atomic number and thus decreasing polarising power and ionic hydration. Generally, less hydrated ions with smaller hydrated radii, such as Na^+ and K^+, are more strongly attracted to charged mineral surfaces. Cation valency is the second major controlling factor on the order of exchange, with multivalent ions being more strongly retained than monovalent ions (Ross, 1989). Clearly cation exchange and selectivity on mineral surfaces are significant in helping to explain physicochemical changes due to

chemical treatment and indeed the early improvements induced by the addition of stabilizers.

2.4 Sources of Impurities

There are considerable amount of weak clay deposits at different parts of the world. The composition and soil characteristics in these areas are inherently site specific as well as historically specific. Therefore the stabilization approach for improving soil properties must be considered in a site specific manner. Furthermore, the sheer variability in the number of impurities present in natural soil shows that there can never really be a unique stabilizing agent. This is because the mixtures of impurities within a soil matrix can create a very complex chemical environment from which their removal is very expensive if indeed possible. Consequently, any remediation technique must be considered carefully meeting the required standards. Some of the more common type of impurities encountered in natural soils are described briefly in the following sections.

2.4.1 Soil Organic Matter

Soil organic matter is complex both chemically and physically, and many reactions and interactions between the soil and the organic matter are possible. It can also be responsible for the high plasticity, high shrinkage, high compressibility, low hydraulic conductivity, and low strength observed in soft soil deposits. In residual soils organic matter is most abundant in the surface horizons. The specific properties of these particles vary greatly depending upon parent material, climate, and stage of decomposition. Notwithstanding its low content, organic matter is a very important soil constituent. It affects the physical and chemical properties of soils. For instance, the results of several investigations have suggested that organic matter content mainly determines soil cation exchange capacity in topsoils, with clay content mainly responsible for the cation exchange capacity of subsoils. Also, it should be noted that

only clay particles can generate a positively charged surface when the soil is acidic, while both clay and organic particles will have negatively charged surfaces when the soil solution is alkaline.

2.4.2 Sulfate Content

The detailed chemistry of the reactions between the lime, sulfates and soil mineral is very complex and depends greatly on the soil pH, temperature and water conditions (Rogers, 1996). What has been established is that, where substantial swelling of lime stabilized material takes place, it is associated with the formation of the mineral ettringite, one of the calcium-aluminum-sulfate hydrates. The hydration of ettringite is accompanied by large dimensional changes as the water of crystallisation is incorporated into the mineral structure. Ettringite often occur as long needle-like crystals and, where the interparticle clay bonding is weak and the ambient stresses are low, these crystals can push apart the clay particles. According to Hunter (1988), once ettringite has started to form it continues to grow, provided that the necessary conditions and constituents remain available. Then provided that the pH value remains high, the dissolution of any available carbonates together with available silica allows a substitution of silica for alumina and carbonate for sulfate leading to conversion from ettringite to thaumasite, a mineral with similar expansive properties to ettringite. The work of Sherwood (1962) also reported that the formation of ettringite is responsible for the disintegration of lime-stabilized soils.

2.5 Chemical Stabilization

In recent years the use of chemical additives to improve soil properties has grown rapidly in many countries. Significant improvements that may be achieved are decrease in the plasticity, shrink-swell potential and an increase in the workability and strength of the soil. These beneficial changes are mainly due to the chemical reactions which take place between the added reactant and soil particles. Many

researches have been conducted to further delineate the nature of these reactions. Generally, stabilization techniques can be classified according to the main stabilizing agent added. They can be categorized based on cement/lime, pozzolana, ionic, enzyme or polymer stabilizers. The results of these investigations for two types of stabilizers, i.e., lime and phosphoric acid are summarized in the following sections.

2.5.1 Lime Stabilization

The use of lime, as chemical additive, to improve soil properties is over 5000 years old, the first record of the process dating back to roman times. For instance, the pyramids of Shensi in Tibet were built using compacted mixtures of clay and lime (Rogers, 1996). Also lime stabilized earth roads were used in ancient Mesopotamia and Egypt. Today treatment of clayey soils by addition of lime is a technique widely used. It is used to improve the bearing capacity of layers in highway, railroad, and airport constructions, as foundation for light structures, as backfill for retaining walls, and as lateral support in excavations and trenches. In addition, with the growing concern for the environment, lime stabilization is also of great interest in lining landfills in order to isolate hazardous and other types of waste materials from the surrounding environment. Therefore, because of the proven versatility of lime stabilization, the method has gained a wider acceptance in different countries of the world and more recently in Southeast Asia. Nevertheless, the acidic nature of tropical soils dictated by the extreme weathering conditions have raised doubts about the efficiency and chemical nature of soil-chemical reactions in an acidic environment and hence their long-term improvement. Some fundamental concepts of lime stabilization are discussed below.

2.5.1.1 Lime Types

The materials that are used in lime stabilization technique are lime, soil, and water. It is important that the type of lime to be used is clearly defined, because the efficiency of process depends in part on the type of lime material used. In general, lime is produced from natural limestone and the particular type of lime formed depends upon the parent material and the production process. In practice, the most commonly used forms in soil stabilization are quicklime (burnt lime) and hydrated lime (slaked lime). Quicklime is produced by heating limestone to about 850^{o}C and driving off carbon dioxide through reactions such as the following:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \uparrow \quad (2.4)$$

When calcium oxide (quicklime) is added to a clay soil the following dehydration reaction takes place:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat} \quad (2.5)$$

Since this reaction is strongly exothermic (65 Kj/mol is generated), water will be driven off due to the rise in soil temperature which sometimes can be so high that the pore water starts to boil. Hence quicklime is suitable for stabilization of clayey soils with moderately high water contents. However, because of its lumpy condition and high heat of hydration, quicklime is caustic to handle, particularly in humid climates. So it is usual to slake the quicklime by adding hot water to form very fine white powders of calcium hydroxide.

Throughout these years, the effect of lime on the stabilization process has been examined by many investigators who have tested various soils with different mixtures of lime. The results obtained have shown that either quicklime or hydrated lime can be used for soil stabilization depending on the soil type and environmental conditions. For instance, according to Greaves (1996), quicklime is more widely used in Britain than hydrated lime, because of it denser state, less dusty nature, and

also due to its hydration and evaporation reactions which makes it more effective when dealing with high moisture content soils. In addition, Laguros *et al*. (1956) have shown that the use of quicklime in treating fine sands and loessal soils is much more effective than hydrated lime. However, despite the efficiency of quicklime in these cases, hydrated lime is the most widely form of lime used for soil stabilization.

2.5.1.2 Soil Types Suitable for Lime Application

In general according to Little *et al*. (1995), soils having plasticity index more than 10 percent and clay fraction greater than 25 percent are suitable for lime treatment. The major soil characteristics which affect soil's reactivity are pH, mineralogy, type of exchangeable cations, carbonate content, extractable iron and degree of weathering.

Berube *et al*. (1990) reported the results of a series of tests conducted on range of soil minerals treated with lime in order to assess their reactivity. The results indicated that reactivity is greatly dependent on the nature of minerals. For instance, siliceous minerals react more with lime than iron or magnesium silicates such as chlorite that can reduce the efficiency of lime treatment. Furthermore, the solubility of the minerals would be expected to increase with decreasing particle size and decreasing degree of crystallinity because of a greater specific surface and less resistant crystal structure. Hence minerals having a three layer structure such as montmorillonite are usually more soluble than minerals having a two layer structure such as kaolinite. This is in agreement with Lees *et al*. (1982) findings who showed that in terms of strength, lime treatment has a greater effect in montmorillonite than kaolinite soils. It should be noted that the cation exchange capacity of a soil is not a criterion for its reactivity with lime. Brandl (1981) suggested that the amount of semi-removable silica or alumina is a useful criterion for lime reactivity which can be used in practical purposes.

Tropical soils have significant differences from soils of other climatic conditions as they have been generated under high temperatures and humid environments. For instance, the acidic nature of these soils has caused a rather conflicting outcome regarding the effectiveness of lime treatment technique. On the other hand, the condition is exacerbated by the dominance of free oxides in these deposits. Nonetheless, it is unclear whether the pozzolanic reactions would be inhibited by the presence of these oxides, and in particular whether a continuous cemented structure will be formed in these acidic environments. This is because of the lack of literature published on the Physicochemical behavior of lime stabilized tropical soils.

2.5.1.3 Lime Content

Soil texture, plasticity changes, and strength development are the three primary factors that indicate lime modification and stabilization have taken place in a soil. The latter being highly dependent on the pH and quantity of calcium ions present in the soil. According to Bell (1996), when lime is added to a clay soil it must first satisfy the short term cation exchange reactions and will not trigger any pozzolanic reactions until the full modification is met. This threshold value has been called by McCallister and Petry (1992) the lime modification optimum, below which only flocculation occurs and above which pozzolanic reactions are possible. Also it is defined as the point at which with further addition of lime, no appreciable increase in plastic limit is observed. In ascertaining the optimum lime content for strength increase, Eades and Grim (1966) have suggested that the lowest percentage of lime required to maintain a pH of 12.4 to be recognized as the percentage required for soil stabilization. This value is known as initial consumption of lime (ICL) in British Standard. According to Ingles (1972) a good rule of thumb in practice is to allow 1 percent by weight of lime for each 10 percent of clay in the soil. Hilt and Davidson (1960) gave a correlation which showed that the amount of lime fixation is in proportion to the type and amount of clay present and is independent of the adsorbed cations.

This relation is given as:

Optimum Lime Content = ((Clay fraction (%)/35) + 1.25 (2.6)

One further point of importance is the fact that, strength does not increase linearly with lime content and excessive addition of lime would reduce the strength. This is due to the fact that, lime itself has neither appreciable friction nor cohesion. In addition the amount of reduction in maximum dry density and the induced carbonation tend to rise with increasing lime content, contributing to more decrease in soil strength. This practically has been examined by Bell (1996) who studied the effect of lime content on the strength development of most frequently occurring minerals in clay deposits. It was found that, minerals mixed with a low lime content attained maximum strength in less time than one to which a higher content of lime had been added.

2.5.1.4 Curing Conditions

Among the different variables affecting the strength of chemically stabilized soils, curing is of major importance. Its effect on the strength is a function of time, temperature and relative humidity (Mitchell and Hooper, 1961).

Several attempts have been made to express the effect of curing time on the engineering properties of fine-grained soils. According to Ingles *et al*. (1972), the prolonged curing of soil-lime mixtures is recognized to favor the pozzolanic reactions. In addition, based on their findings increasing curing temperature would promote growth and crystallization of any amorphous reaction products which may be forming. According to Arabi and Wild (1986), the variation in unconfined compressive strength at room temperatures is negligible, while increasing sharply with increasing temperature.

2.5.1.5 Soil-Lime Interaction

In general, soil-lime reactions can be divided into two distinct phases known as modification and stabilization.

The modification phase refers to the process that occurs immediately after introducing lime into the clay environment, causing considerable changes to the texture of the soil. These changes which occur to some extent with all lime treated soils are clearly visible in the laboratory or on site, since they are dramatic and virtually instantaneous. As mentioned in previous sections, the thickness of the diffused double water layer is greatly dependent upon the type and concentration of cations available in the pore water. When lime is added to a clay soil, the divalent calcium cations present in the solution can easily replace the unfriendly monovalent exchangeable cations that are adsorbed on the surface of clay lattice, thus causing alteration in the density of electrical charges around the clay particles known as the zeta potential and moreover a sharp reduction in the repulsive diffuse double layer forces. This would lead to closer proximity of clay particles and their edge to face attraction, the process being termed flocculation. It is this process which is primarily responsible for the modification of engineering properties of clay soil when they are treated with lime. Nevertheless the ability of clay to undergo these changes is not necessarily a determinant factor. In another words, although calcium saturation (full modification) is required for stabilization, if a soil is non-reactive, extensive pozzolanic strength development will not be achieved regardless of lime type or curing conditions. The net result of cation exchange and flocculation and their effect on the structure and behavior of clayey soils are as follows (Rogers, 1996):

a) Considerable decrease in susceptibility of clay to moisture changes which is caused by sharp reduction in the thickness of the diffuse double layer.

b) Transformation of soil structure into larger sized aggregates or clusters.

c) Increased internal friction among the agglomerates as a result of flocculated structure.

d) More enhance workability due to the textural changes from a plate-like plastic clay to a friable, needle-like material.

The reactions which take place after the modification phase are time dependent and continue for a long period of time. Among the various mechanisms which are responsible for the soil improvement, the pozzolanic reaction is believed to be the main phenomena for insuring an effective lime stabilization. This reaction involves the interaction between soil silica and/or alumina (natural pozzolans) and calcium hydroxide to form various types of cementing agents that bonds soil particles together.

In general, pozzolans are defined as finely divided sources of silica or alumina which are present for hydration by alkali or alkali earth hydroxides to form cementitious products in the presence of moisture at ordinary room temperatures. In soils sources of silica and alumina are numerous such as clay minerals, quartz, and amorphous forms of silica and alumina. Therefore in a clay-lime-water system with a high pH environment to solubilize silica and alumina for the pozzolanic reaction, as long as enough residual calcium ions are present in the system and the highly alkaline conditions persist, the following reactions will continue to occur (Little, 1995):

$$Ca^{++} + OH^{-} + \text{Clay Silica} \rightarrow \text{Calcium Silicate Hydrate (CSH)}$$

$$Ca^{++} + OH^{-} + \text{Clay Alumina} \rightarrow \text{Calcium Aluminate Hydrate (CAH)} \qquad (2.7)$$

These water insoluble gels of calcium silicate and aluminate hydrates contribute to flocculation by coating and bonding adjacent soil particles together and as curing occurs they strengthen the soil. It should be noted that at the early stages of the reaction these cementitious products are often poorly crystalline and amorphous in nature.

Another mechanism which is often observed in soil-lime mixtures is lime carbonation. In this process, lime reacts with the carbon dioxide in the atmosphere or in the soil to form relatively weak cementing agents such as calcium carbonate. According to Diamond and Kinter (1965) this is an undesirable reaction since it consumes part of the lime that would normally be used to form more resistant cementing products. In addition Eades and Grim (1966) have demonstrated that the strength gain in soils due to cementation caused by carbonation is rather negligible.

Glendinning (1995) compiled observations of a number of researchers investigating the addition of lime and suggested reaction mechanisms to help explain changes in the behaviour of lime treated clayey soils. The results are presented in Table 2.3.

2.5.1.6 Lime Stabilization Limits

The increase in strength of lime stabilized soils has been reported by many researchers (Balasubramaniam *et al*., 1989; Locat *et al*., 1990; Bell, 1996; Narasimha Rao and Rajasekaran, 1996). Nonetheless, the use of lime as a stabilizer can bring unfavorable changes to other soil properties. For instance, the test results of Clare and Cruchley (1957) indicated that there was a decrease in plasticity of soils after lime stabilization. Some researchers also found that lime treatment contributed to the brittle failure characteristics of soils that led to a rapid and great loss in strength when failure occured (Sabry *et al*., 1996). Also the phenomenon of sulfate-induced heave has received much attention during the past decades and continues to pose problems for lime stabilized soils that contain considerable amount of soluble sulfates (Sherwood, 1962; Hunter, 1988; Mitchell and Dermatas, 1992; Kota *et al*. 1996; Rollings *et al*., 1999). Furthermore, as was stated before, the acidic nature of tropical soils and also the presence of free oxides have raised concerns regarding the efficiency and chemical nature of soil-lime reactions and hence their long-term improvement.

Table 2.3 : Summary of soil-lime reaction mechanisms (Glendinning, 1995)

Author	Observation	Suggested Mechanism
Brandl (1981). Mateos (1964).	Swelling potential/pressures reduced.	Formation of cementitious compounds that form interlocking compounds.
Eades and Grim (1966).	Formation of calcium aluminate hydrates/silicate hydrates at high pH (high lime content).	High pH induces solubility of silicates and aluminates in the clay, hence reaction able to occur.
Diamond and Kinter (1965).	Formation of new products	Lime adsorption leads to reaction at clay surfaces, giving rise to precipitate reaction.
Harty and Thomson (1973).	Greater improvements with highly weathered soils.	Weathering increases clay susceptibility to dissolution of silica and alumina.
Quigley and DiNaro (1978).	Greater improvements using high lime contents on weathered soil than non-weathered.	Weathering increases smectite content that reacts via a different mechanism.
Moore and Jones (1971).	Reactivity greatly reduced with high iron content.	Iron in the form of positively charged aggregations reducing ion-exchange capacity.
Mateos (1964).	Lesser degree of improvement using illite and chlorite than montmorillonite.	Cation exchange capacity reduced.
	Higher increases in plastic limit with increasing clay content.	Clay is the reactive clay constituent.
Bell (1988).	Kaolinite + 2% lime, liquid limit rise; kaolinite +< 2% lime liquid limit falls.	Particle surfaces modified by the action of hydroxyl ions.

Table 2.3 : Summary of soil-lime reaction mechanisms (continue)

Author	Observation	Suggested Mechanism
Newman (1987).	Flocculation.	Cation exchange leading to reduction of double layer.
Diamond and Kinter (1965).	Flocculation in calcium saturated clay. Changes in plasticity, shrinkage and swelling. Increase in strength.	Formation of small amounts of cementitious material at points of contact.
Lees *et al.* (1982).	Clay + 2% lime addition gives sharp increase in Φ.	Modification by flocculation and particle rearrangement.
Hilt and Davidson (1960).	Limitation to the increase in plastic limit with addition of more lime.	Lime-fixation-crowding of cations within clay structure.
Diamond and Kinter (1965).	Limitation of lime taken out of solution, Ca in same proportion as hydroxyl ions. No overall charge change. Able to wash out. No heat given off.	Physical absorption of lime – a single molecular layer of $Ca(OH)_2$.
	Increased adsorption. Not able to fully wash out.	Chemical reaction at contact points.
Bell (1988).	Non-linear relationship between lime % and strength gain after 2% addition for montmorillonite; 2-4% for kaolinite.	The existence of an optimum addition of lime.
Lees *at al.* (1982).	Decrease in Φ for kaolinite with increases for lime addition over 2%.	Optimum lime addition/particle rearrangement dominant stabilising factor.
	No decrease in strength with larger additions of lime to montmorillonite.	Pozzolanic reactions dominant stabilising factor.
Bell (1988).	Decrease in maximum dry density.	Formation of cementitious compounds that form interlocking compounds.

Table 2.3 : Summary of soil-lime reaction mechanisms (continue)

Author	Observation	Suggested Mechanism
Bell (1988).	Higher compaction densities obtained in kaolinite than montmorillonite.	Expandable minerals have greater affinity for water due to shape and higher specific surface.
Lees *et al*(1982).	No clear optimum of moisture content-dry density compaction curve- most noticeable in montmorillonite	Initial formation of cementitious compounds affects compactibility-montmorillonite most reactive.
Bell (1988).	Dramatic immediate increase in the unconfined compressive strength with small lime addition in montmorillonite.	Expansive clays react more quickly due to greater cation exchange capacity.
Lees *et al*(1988).	Cohesion and unconfined compressive strength correlation.	Both affected by the same part of the mechanism.

2.5.2 Phosphoric Acid Stabilization

In the past decades, depending on the nature and function of the soil, many different liquid stabilizers have been proposed. However the use of acidic additives such as phosphoric acid has been extremely limited. Although they have been used effectively on some roads in North America (The Missouri State Highway Department), but unfortunately due to their higher cost in comparison to the commercial alkali additives such as lime, their treatment has been regarded as too expensive. According to Ingles (1972), there are two particular advantages in the use of phosphoric acid or phosphate compounds in soil stabilization. First, the troublesome clay mineral chlorite which shows a deleterious behavior in lime or cement treated soils has been observed to react well with phosphoric acid and second, the initial dispersive action of the phosphate ions on clay particles is a considerable aid to densification, causing noticeable improvement in the strength of

stabilized soil. On the other hand, the use of phosphoric acid in stabilization of tropical soils that contain high amounts of iron and aluminum oxide has shown promising results which might otherwise require costly transportation and replacement of the material.

Kittrick and Jackson (1955) studied the reaction mechanisms of a latosolic soil with phosphate. The soil was mainly comprised of kaolinite mineral and contained considerable amount of iron oxides (18.2%). The results indicated that the soil sample showed a high reaction rate at the early stages of curing. Also the formation of new reaction products in the form of hexagonal and rectangular crystals was observed. According to Michaels and Tausch (1960), the use of phosphoric acid as a stabilizer was effective in improving the properties of moderately plastic clays. Also based on their findings, calcium phosphate (phosphate rock) with sulfuric acid can be used as an efficient phosphate compound for stabilizing lean clay soils.

As stated in the paper published by Medina and Guida (1995), following conclusions based on the findings of a number of researchers investigating on soil stabilization with phosphoric compounds have been made:

a) Most acidic soils that contain an appreciable amount of clay minerals respond well to phosphoric acid treatment.

b) Phosphoric acid reacts with free iron and aluminum oxides, producing heat and rapid formation of insoluble reaction products.

c) Some test results have revealed that sulfuric acid used in conjunction with either phosphate rock or phosphoric acid does result in improved treatments. However, excess sulfuric acid impairs the strength of the cementitious phosphate formed.

d) The effective concentration range of phosphoric acid is 1-5% by weight of the dry soil. A level of 2% may be considered sufficient to bring strength to weak subgrades, but higher levels are probably needed for sub-base and base pavement layers.

e) In stabilizing very plastic clays, the use of trace amounts of some secondary additives (P_2O_5 and octylamine) may be beneficial.

It should be stressed that, although all phosphate additives are non-toxic, there is some difficulty in handling phosphoric acid and the treated soil due to their liquidity and sticky nature, respectively. However the mechanics of modern field mixing techniques applicable to difficult soils has sparked an interest in the improvements that may be possible with locally available soil. Apart from its stabilizing action there are other possible uses of phosphoric acid of appropriate purity. For instance, for the production of active charcoal, adhesives, and also soil fertilizers.

2.5.2.1 Soil Types Suitable for Acid Stabilization

According to Ingles (1972), the use of phosphoric acid for improving soil properties is only limited to low pH soils and is generally ineffective in alkaline soils, silts, and sands. This is because the action of the stabilizer depends upon acid attack on a clay mineral lattice. This is consistent with Lyons *et al*. (1962) findings who have carried out considerable experimenting with phosphoric acid on different types of clay soils with plasticity indexes ranging from 13 to 44. Based on their observations, in a soil with highly alkaline environment and high silt content the acid treatment seems to be ineffective, since the former would neutralize the acid and the latter does not have high content of alumino-silicates which is required to produce the cementing substance.

In general, the soil constituents that posses greater anion exchange capacity have a greater affinity for phosphate ions (Brady and Weil, 1996). For instance, among silicate clays, kaolinite is more reactive with phosphate ions than other clay minerals. Moreover, Demirel *et al*. (1962) have shown that the degree of improvement is highly dependent on the type and amount of clay minerals present in the soil. Based on their findings phosphoric acid appears to be much more reactive

with chlorite minerals than with montmorillonite, illite, and vermicullite type clay minerals. Also they have reported that the presence of calcium carbonate would increase the amount of acid required for the stabilization process due to its neutralizing action before reacting with other soil constituents. On the other hand, in tropical countries aluminum is not necessarily preponderant in soils. Presence of free iron oxides due to the laterization process may be important as well. These soils also have high potential for being stabilized with phosphorous compounds.

2.5.2.2 Phosphoric Acid Type and Content

Phosphoric acid or more precisely orthophosphoric acid, H_3PO_4, is produced from crude phosphates by the wet and thermal decomposition processes. Among these techniques, the former being the most popular by producing 90 percent of the phosphoric acids consumed worldwide. In this process, the crude phosphates are decomposed with mineral acids. Sulfuric acid is preferably used for this purpose, but hydrochloric acid and nitric acid are also used. Although phosphoric acid is miscible with water in all proportions, it is commercially available in only three concentrations (75%, 80%, and 85% H_3PO_4). The overall reaction during production of wet phosphoric acid can be formulated as:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 5xH_2O \rightarrow 5CaSO_4.xH_2O + 3H_3PO_4 + HF \qquad (2.8)$$

(where x = 0, 0.5, 2)

Demirel *et al*. (1962) have suggested that similar to the lime treatment method, there is an optimum amount of phosphoric acid which produces the highest compressive strength in acid stabilized soil. However this point has not been clearly identified in terms of dry weight of the soil. Furthermore, as stated by Medina and Guida (1995), a concentration range of 1-5% phosphoric acid by weight of the dry soil seems to be sufficient in improving the engineering properties of the soil for road construction purposes. It should be stressed that, one of the advantages of using

phosphoric acid instead of a soluble phosphate in soil stabilization is the fact that the hydrogen ion present in the acid helps to dissociate the mineral structure and, therefore, more reactants are mobilized.

Also it is worth noting that, phosphoric acid should not be confused with phosphorous acid (H_3PO_3). A single letter difference in the name of a chemical compound can make a difference in its properties. Phosphorous acid releases the phosphonate ion (HPO_3^{2-}), also called phosphite, upon disassociation.

2.5.2.3 Phosphoric Acid-Soil Reactions

In general acids are effective in removing alumina and other metallic oxides from clay minerals (Herzog and Mitchell, 1963). Two basic phosphate reactions are distinguished with Al and Fe oxides and hydroxides. These reactions differ in the time scale over which they occur and the stability of products formed. The initial reaction appears to be a fast ligand exchange of surface hydroxyl groups with phosphate and the formation of inner-sphere surface complexes (Laiti *et al*., 1996; Nanzyo, 1984; Persson *et al*., 1996). For the longer term reactions, two possible mechanisms have been suggested. The first one involves the slow diffusion of phosphate ion into micropores (van Riemsdijk *et al*., 1984). Another proposed mechanism is the slow weathering of surface in the presence of phosphate and the formation of metal phosphate precipitate (Laiti *et al*., 1996; Lookman *et al*., 1997; Li and Stanforth, 2000).

The following equations can be given as the surface reactions of phosphate ion with kaolinite (Ioannou and Dimirkou, 1997):

$$SOH + H^+ \leftrightarrow SOH_2^+$$

$$SOH \leftrightarrow SO^- + H^+$$

$$SOH + H_3PO_4 \leftrightarrow SH_2PO_4 + H_2O \quad (2.9)$$

$$SOH + H_3PO_4 \leftrightarrow SHPO^- + H_2O + H^+$$

$$SOH + H_3PO_4 \leftrightarrow SPO_4^{-2} + H_2O + 2H^+$$

Where SOH represents the surface functional group of kaolinite. Although all the exact mechanisms have not been identified, however phosphate ions are known to react with iron and aluminum minerals surfaces in several different ways. Some of these reactions are shown diagrammatically in Figure 2.13. As can be seen, the phosphate anions can be attracted to the surfaces of metallic oxides and the broken edges of kaolinite and form phosphorus containing compounds (Brady and Weil, 1996). According to Lyons *et al*. (1962), when soluble phosphoric acid is added to a soil, it tends to undergo sequential reactions with the initially dissolved aluminum, precipitating phosphorus containing compounds. Furthermore, as the time passes, this water soluble salt reacts further to produce a insoluble cementitious gel composed of amorphous aluminum. Thus the overall reaction at room temperature can be given as:

$$Al(OH)_3 \text{ (from the clay lattice)} + 3H_3PO_4 \rightarrow Al(H_2PO_4)_3 + 3H_2O$$

$$2Al(OH)_3 \text{ (from } Al(H_2PO_4)_3) + \text{clay lattice} \rightarrow 3AlPO_4 \text{ (cement gel)} + 6H_2O \quad (2.10)$$

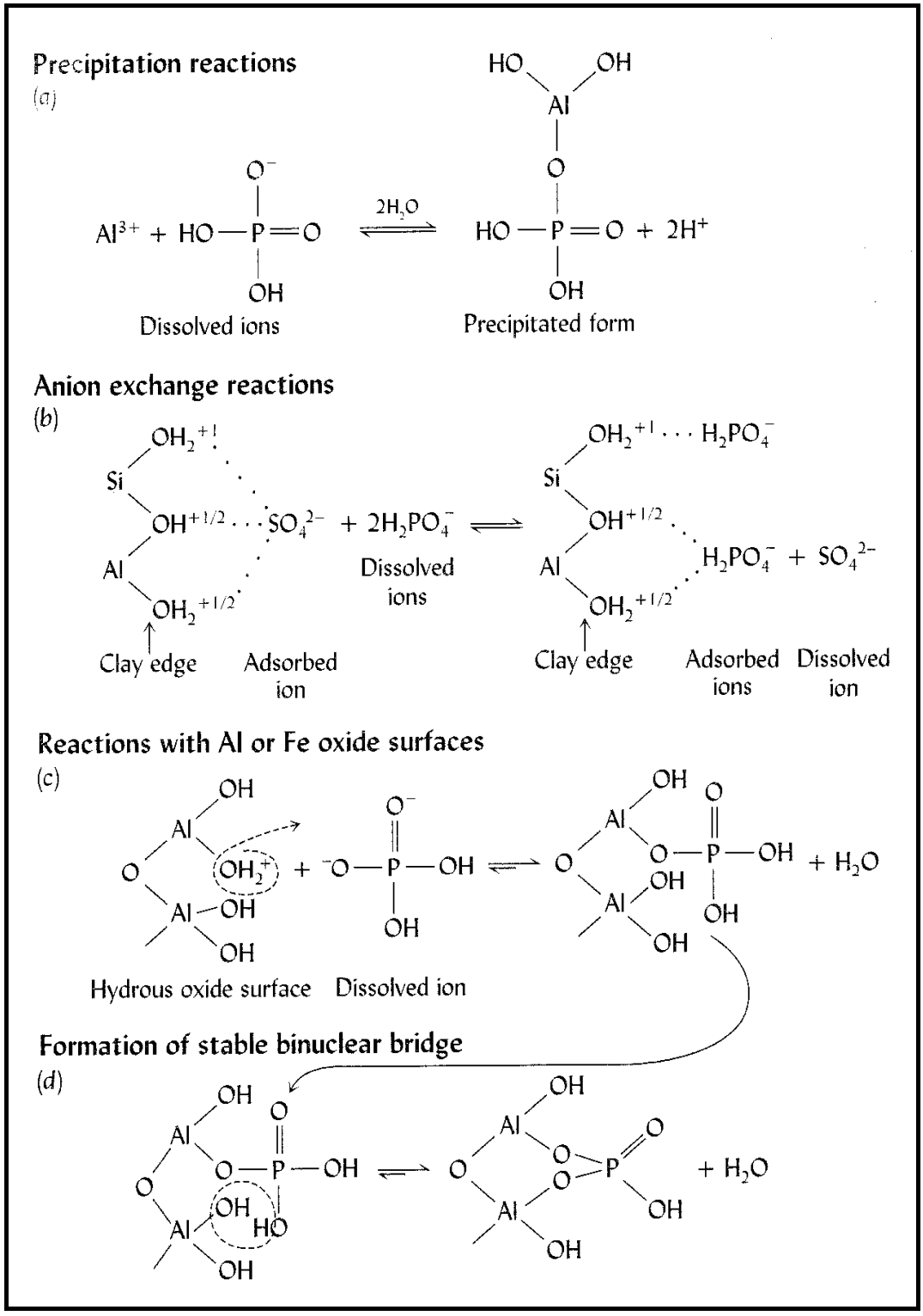


Figure 2.13 Several of the reactions between the phosphate ions and iron and aluminum in various hydrous oxides (Brady and Weil, 1996)

In the paper published by Michaels *et al*. (1958), a more general equation was presented as the reaction outcome between the phosphate compound and soil particles:

$$\begin{array}{ll} \text{Al(soil)} & MPO_4 \\ \updownarrow & H^{+}\updownarrow \\ Al^{3+} + 2OH^{-} + H_2PO_4^{-} + xH_20 \rightarrow & Al(OH)_2.H_2PO_4\,.xH_20 \end{array} \qquad (2.11)$$

A1 (soil) is the aluminum source of the soil, which may be gibbsite ($Al(OH)_3$) or the clay mineral kaolinite, MPO_4 is the phosphate source added to the soil. The final product ($Al(OH)_2.H_2PO_4.xH_2O$) is hard and highly insoluble. A similar reaction exists between the iron content of the soil and the phosphate source. For instance for goethite (Fe_2O_3), the new compound formed is $Fe(OH)_2.H_2PO_4.xH_2O$, which is also hard and highly insoluble.

2.6 In-Situ Methods of Reagent Application

2.6.1 Surface Clay-Reagent Mixing

The usual procedure for surface clay-lime mixing and other cementitious reagents involves spreading the reagent onto the surface and mixing to a depth of 200-400mm using a purpose-built rotavator or standard excavation equipment. This approach is often used to stabilise road foundations and is illustrated in Figure 2.14.

With respect to lime treatment it was traditional practice to allow the clay-lime mix to stand for a period of typically 24 hours in order that complete lime distribution could occur. This process, known as mellowing, was considered vital for full modification of the clay minerals. Current thinking, however, suggests that immediate water content adjustment (where necessary) and compaction is more beneficial in achieving a long-term strength gain (Holt and Freer-Hewish, 1996).

Glendinning *et al*. (1998) also suggested that the compaction of the clay-lime mix is important in achieving the intimacy of contact of the modified clay particles required for the full benefits of the reaction to be obtained. In addition a minimum air void content should be aimed for, since this will again aid the reaction process. For these reasons the water content should be slightly higher than the optimum water content determined for the clay-lime mix and an appropriate level of compaction should be applied to achieve a dry density close to the maximum achievable.

Figure 2.14 Spreading and initial mixing of lime with soil using a rotary mixer

2.6.2 Deep Clay-Reagent Mixing

An alternative in situ treatment for deep deposits is to form reagent columns, which are cylindrical columns of stabilizing reagent mixed with clay typically 0.5-1.0m in diameter.

The process of deep in situ soil stabilization was described by Higgins (1965). On the other hand, the technique for lime columns was developed in Sweden (Broms & Boman, 1976) for stiffening and strengthening soft and wet clayey soils. In this technique, a lime content of typically 10% is used with the lime being incorporated through the stem of an auger that is first driven into the ground to an appropriate depth. The rotation of the auger is reversed as the lime is fed into the soil, causing mixing and a degree of compaction (Figure 2.15).

Figure 2.15 Deep clay-reagent mixing

2.7 Chemical Analysis of the Stabilized Soil

The chemical analysis performed on the treated samples is to assess the time-dependent changes induced on the structure of soil-stabilizer matrix. Also it is used to detect and determine the chemical composition of the new formed products. The methods adopted for monitoring these changes can be divided into three main categories:

a) First of all, it is important to determine the type of minerals and elements that are present in the soil structure. This is usually regarded as micro-structural characterization and can be carried out by using spectroscopic techniques such as X-ray Diffraction (XRD). Also, in order to observe the morphological changes induced on the fabric of stabilized soil and in particular the subtle formation of amorphous compounds, microscopic techniques such as scanning electron microscopy (SEM) are considered to be most suitable.

b) The second category of analysis known as molecular characterization attempts to investigate the effects of chemical stabilizers on the molecular structure and bonding of clay particles.

c) Finally, it is important to determine which elements and compounds are present in the pore water via performing leaching analysis. Also, it is aimed to monitor the release of clay silica and/or alumina and the consumption of stabilizing agents during the stabilization process.

2.7.1 Micro-Structural Characterization

2.7.1.1 X-ray Diffraction Studies

X-ray Diffraction (XRD) is one of the most widely primary investigative techniques used in stabilized soils. This is because the method is easy and produces a great deal of rapidly interpretable information on many aspects of the soil structure.

The mineralogical changes associated with lime stabilization of various clayey soils from Eastern Canada were studied by Choquette *et al*. (1987). The XRD analysis was performed on treated samples after 0, 30, and 300 days of curing. The results indicated that, all intensities of clay mineral reflections decreased with time. This was in good agreement with other researches conducted in this field. For instance, according to Bell (1996), when kaolinite was treated with varying increments of lime, the intensity of its peaks was both decreased and broadened. Based on his observation, the vigorous action and the flocculating effect of lime in the alkaline environment attributed to such behavior. Furthermore, he stated that new reflections were visible at various d-spacings which indicated that new reaction products had been formed. These new compounds were calcium silicate hydrates (CSH) in the form of tobermorite and afwillite and calcium aluminate hydrates (CAH) of the form C_4AH_{13}, CAH_{10}, and C_3AH_{11}. Similar XRD analysis was carried out by other investigators such as Diamond and Kinter (1965), Sabry *et al.* (1981), and Berbue *et al.* (1990) who also reported the presence of CSH and CAH reaction products. Furthermore, as stated by Rao and Rajasekaran (1996), the new CAH compounds were believed to have been formed as a result of the reaction of lime with kaolinite minerals. Similarly, the compounds CSH were believed to have been formed due to lime-montmorillonite reactions (Figure 2.16). Bell (1996) also reported the formation of CSH in lime-quartz mixtures.

The X-ray diffractogram of the natural and acid treated smectite is shown in Figure 2.17. According to Rodrigues (2003), after the acid treatment, an alteration in the crystallization states of montmorillonite mineral was evident. Apparently, as reported by many researchers, the phyllosilicates are the principal minerals that are attacked in an acidic and basic environment and consequently, they are the primary source of silica and alumina necessary for the formation of cementing agents. Moreover, the intensities of various new formed compounds are improved with increasing curing time which indicates that these cementitious products are gradually converted to well crystallize phases from an initial gel state. However, apart from these products, there can be several other non-crystalline products which are not identified by XRD technique. In fact, there are certain inherent weaknesses in the

XRD method. According to Choquette *et al.* (1987), there are three major factors that influence the detection of new formed phases:

a) The weak reflection of new phases due to the poor crystalline structure.

b) The presence of many distinct new minerals as a result of great variety in their chemical composition.

c) Finally, the overlap between the reflection of these minerals with those of primary minerals.

Also as stated by Wild and Arabi (1989), many of the cementitious materials are produced in an extremely finely divided state which results in very diffuse x-ray reflections. Therefore it can be very misleading to identify soil-chemical reaction products only based on the results obtained from XRD technique.

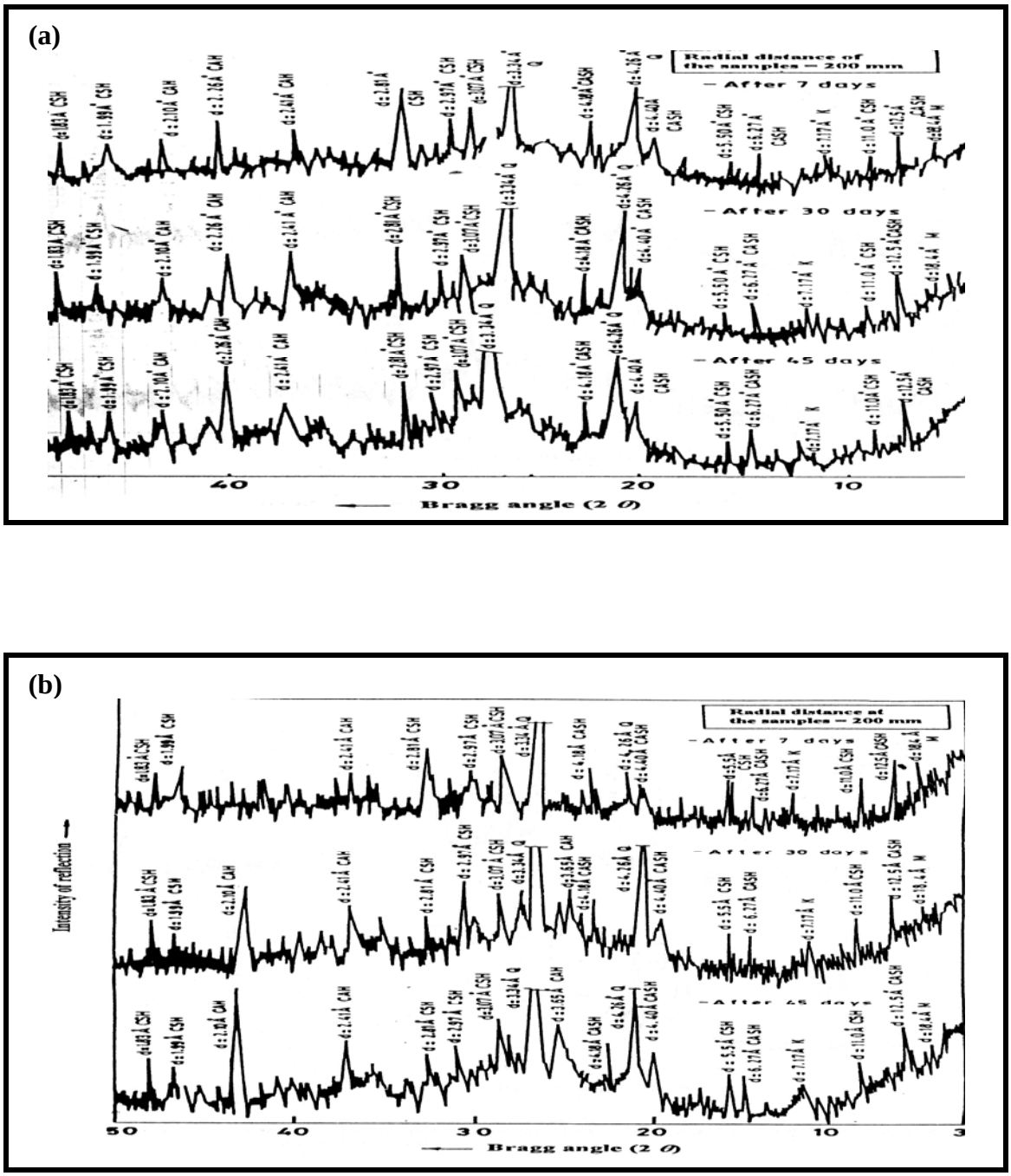


Figure 2.16 XRD patterns of lime treated samples in (a) fresh water and (b) sea water setup (Rao and Rajasekaran, 1996)

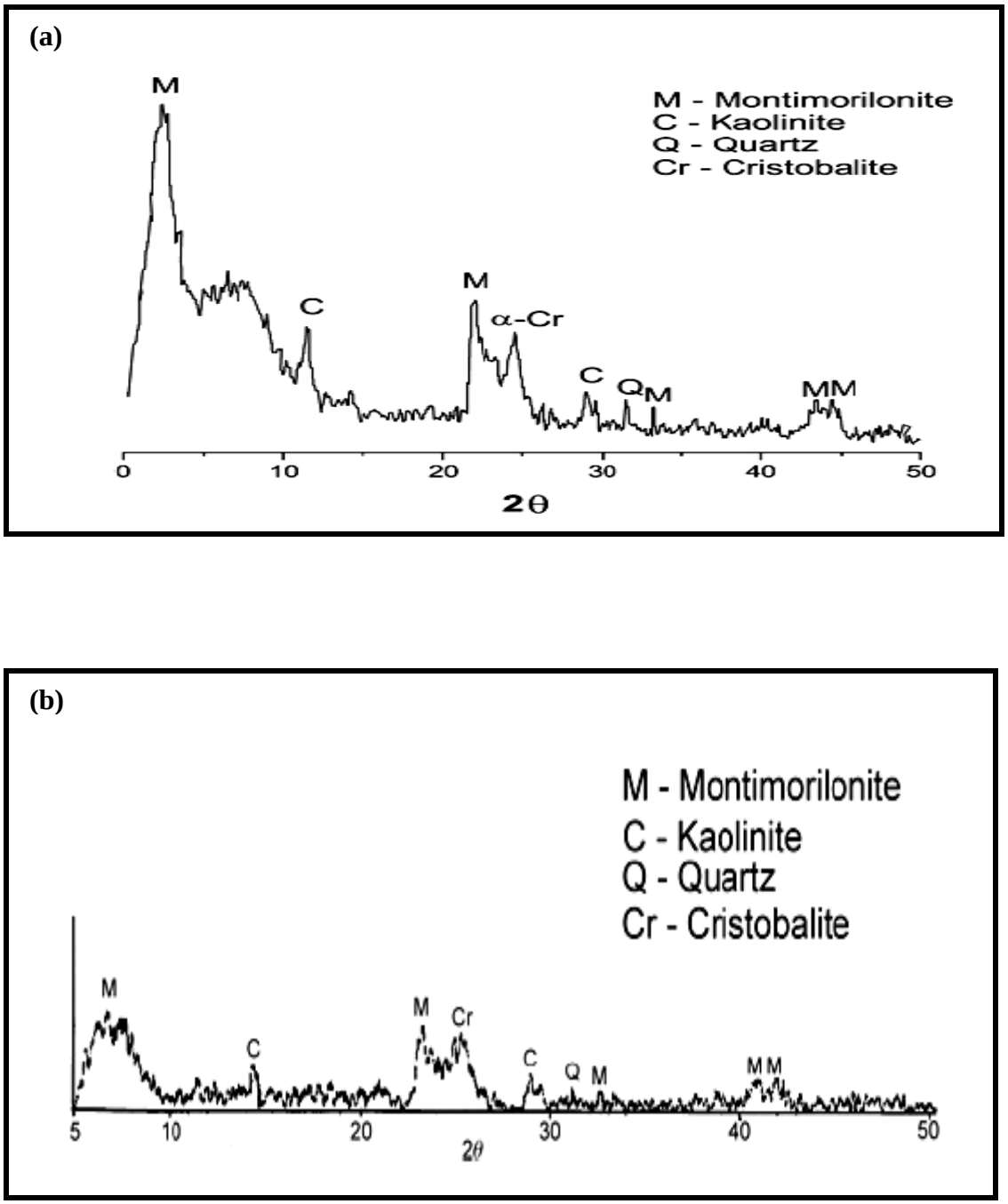


Figure 2.17 X-ray Diffractogram of the (a) natural and (b) acid treated smectite clay (Rodrigues, 2003)

2.7.1.2 Microscopic Studies

Scanning Electron Microscopy (SEM) is a common technique used to view the micro-textural features of soil matrix as exposed on its surface, providing information on the size, shape, and the state of orientation and aggregation of soil particles. This method has been carried out in many lime stabilization studies, in order to visualize the changes occurring in different soil minerals and moreover to observe the formation of new cementitious materials that are not detected in the XRD method. In addition with the help of an Energy Dispersive X-ray Analyser (EDAX) coupled to the SEM, it is possible to determine the elemental composition of these products.

According to Cai *et al*. (2006) findings, when lime is initially mixed with dried clayey soil, the behavior of clay particles towards water is transformed to hydrophobic. Thus, it becomes difficult for the soil particles to form big aggregates when water is added to the lime–soil admixture.

Figure 2.18 demonstrates the mineralogical and morphological changes taking place in a lime stabilized Buckingham soil conducted by Choquette *et al.* (1987). As can be seen in image (A), the untreated soil in its remolded state exhibits an overall open microstructure. The texture of the same soil after 4 percent addition of quicklime is shown in image (B). It is clearly evident that due to the short term reactions (exothermic hydration process, cation exchange, and flocculation) the soil particles have transformed into larger lumps and also the flaky texture has almost completely disappeared. Furthermore, as the pozzolanic reaction proceeds (Images (C)-(F)), the newly formed lamellar and reticular phases have coated and bonded the soil particles together. By means of an Energy Dispersive Spectrometer (EDS), these phases were roughly identified as CASH and CSH, respectively. Thus it appears that in the long term, the strength development of lime stabilized clayey soils is strongly dependent on the continuous formation of new cementing products.

According to Berube *et al*. (1990), there is a significant relationship between cementing capacity and texture of new formed phases. A reticular texture observed preferentially with the CSH provides better cementation power than a fibrous or platy CASH texture, the former allowing much more contact between the soil particles. Arabi and Wild (1986) also reported the formation of CSH and CAH in the mixture of red marl with lime. According to their findings before and after treatment, there are clear evidence of morphology changes at the surface and edges of the soil particles. Furthermore, with increasing curing time, there are sufficient cementitious materials available to form bridges between the adjacent soil particles which would eventually develop into a dense mat of plate-like materials.

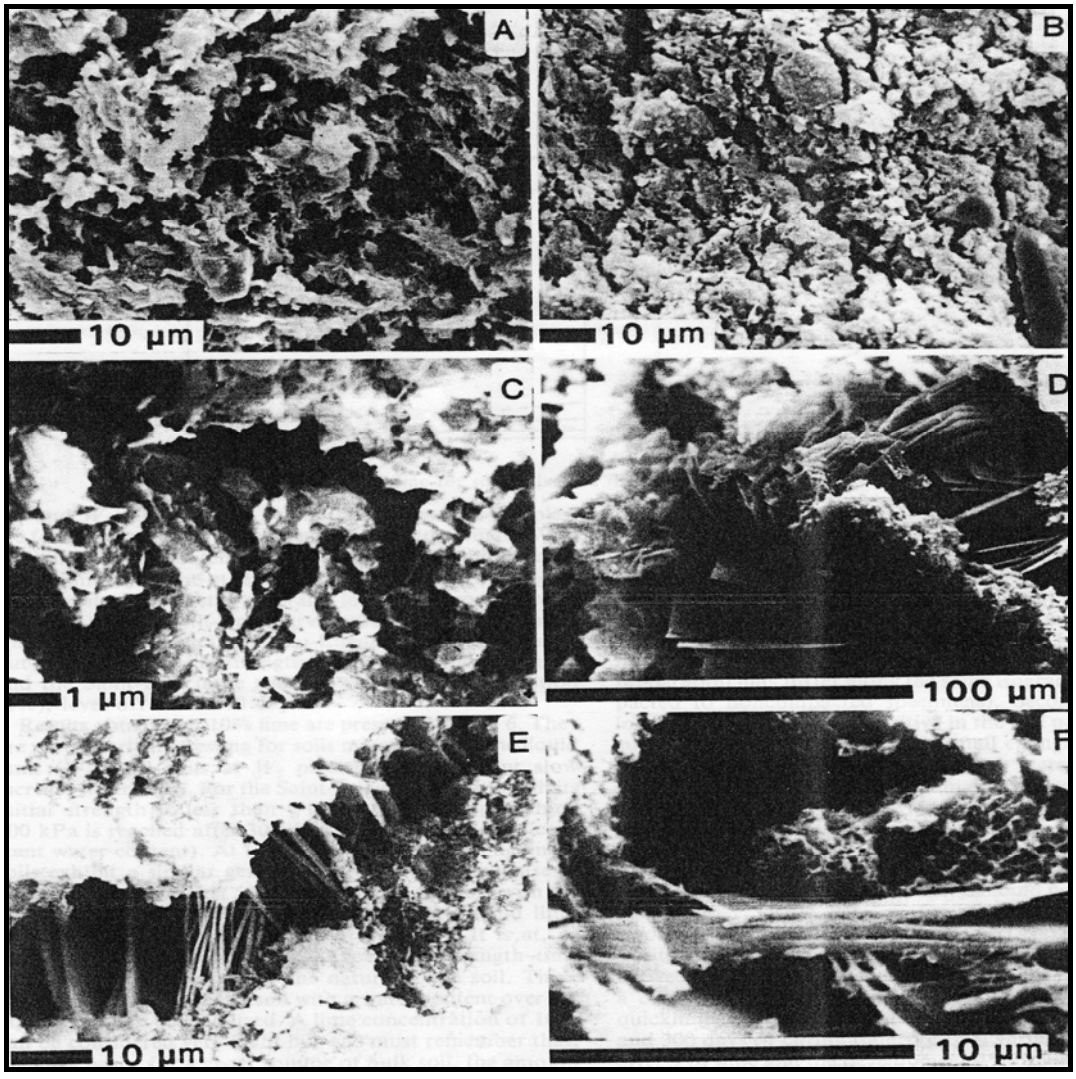


Figure 2.18 Scanning electron micrographs of lime treated Buckingham soil (Choquette *et al*., 1987)

2.7.2 Thermal Studies

Thermal analysis involves a dynamic phenomenological approach to the study of soils by observing its response to a change in temperature. The results for this type of analysis can be obtained in three different ways, i.e., thermal gravimetric analysis (TGA), Differential thermal analysis (DTA), and derivative thermal gravimetric (DTG) analysis.

In Table 2.4, TGA, DTG, and DTA analysis for more commonly available clay minerals are presented. As shown, for clays, endothermic reactions involve desorption of surface H_2O, dehydration at low temperatures, dehydroxylation and eventually melting at more elevated temperatures. Exothermic reactions are related to recrystallization at high temperatures that may be nearly concurrent with or after dehydroxylation and melting.

Figure 2.19, illustrates the TGA and DTG curves of natural and lime stabilized Winn Rock soil. As can be seen, Gypsum dehydration spans the temperature range between 98ºC and 116ºC, with the maximum dehydration occurring at 105ºC. The peak at around 400ºC best corresponds to kaolinite. The thermal analysis patterns of the lime treated soil shows how gypsum reacts with lime. As can be seen, at the early stages of curing, considerable amounts of lime and gypsum are still present. However, by the end of three months curing, the lime peak cannot be detected and the gypsum peak is barely detectable.

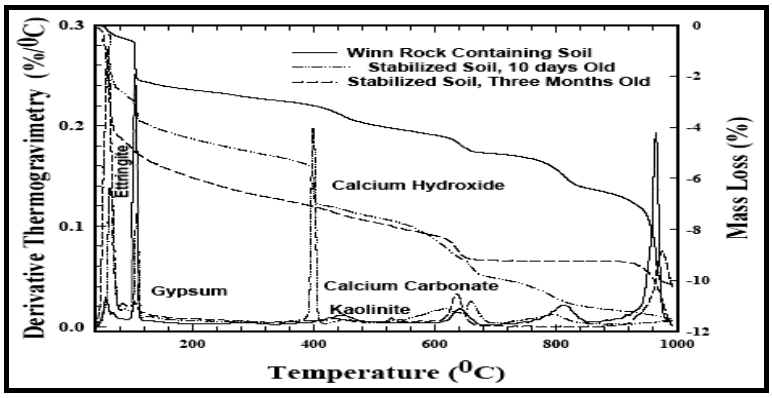


Figure 2.19 TGA and DTG curves of Winn Rock soil stabilized with lime (Roy *et al*., 2003)

Table 2.4 : TGA, DTG, and DTA analysis for more commonly available clay minerals (Guggenheim and van Groos, 2001)

TGA analysis

Sample	Adsorbed water/Dehydration/Other									Other			Dehydroxylation					
	To	Tc	Δ wt.%	To	Tc	Δ wt.%	To	Tc	Δ wt. %	To	Tc	Δ wt.%	To	Tc	Δ wt.%	To	Tc	Δ wt.%
KGa-1b*	<20	—	—	—	—	—	—	—	—	—	469	0.40	468	567	12.66[a]	—	—	—
KGa-1b^	<20	—	—	—	—	—	—	—	—	—	474	1.68	474	566	12.26[a]	—	—	—
KGa-2*	<20	—	—	—	—	—	—	—	—	—	457	0.55	457	541	12.08[a]	—	—	—
KGa-2^	<20	—	—	—	—	—	—	—	—	—	462	2.07	462	561	12.19[a]	—	—	—
SWy-2^	<20	69	6.22	69	151	1.32	—	—	—	151	631	1.70	631	719	3.20	—	—	—
SWy-2″	<20	74	8.26	74	158	1.46	—	—	—	158	619	1.39	619	713	3.47	—	—	—
SAz-1*	<20	90	7.39	90	155	2.80	—	—	—	155	541	1.05	541	683	2.93	—	—	—
SAz-1^	<20	100	13.65	100	165	3.90	—	—	—	165	575	2.01	575	674	2.44	—	—	—
SAz-1″	<20	92	15.22	92	162	4.00	—	—	—	162	567	2.32	567	666	2.82	—	—	—
STx-1*	<20	107	5.04	107	173	7.40	—	—	—	173	598	1.00	598	709	2.73	—	—	—
STx-1^	<20	93	10.61	93	165	2.66	—	—	—	165	617	1.45	617	706	2.63	—	—	—
STx-1″	<20	76	8.97	76	148	2.89	—	—	—	148	545	1.82	545	703	2.89	—	—	—
Syn-1^	<20	70	3.81	—	—	—	—	—	—	70	409	2.69	409	531	4.81	531	643	2.72
Syn-1″	<20	64	5.01	—	—	—	—	—	—	64	408	2.75	408	523	4.81	523	639	2.66
SHCa-1^	<20	78	7.85	—	—	—	—	—	—	78	562	1.62	562	658	0.64	858	711	0.19
SHCa-1″	<20	73	6.70	—	—	—	—	—	—	73	564	1.70	564	717	1.20	717	743	0.60
PFl-1*	<20	71	2.12	71	115	4.73	187	245	2.24	245	361	0.49	361	506	4.30	—	—	—
PFl-1^	<20	64	3.92	64	97	4.31	191	247	2.20	247	382	1.01	382	497	3.77	—	—	—
PFl-1″	<20	86	6.33	86	170	1.51	170	220	2.37	220	354	0.94	354	510	4.53	—	—	—

DTG analysis

Sample	Adsorbed water/Dehydration															Dehydroxylation						
	Peak (1)									Peak (2)												
	Po	Sm	Sr	Pm	So1	Sm1	So2	Sm2	Pr	Po	Sm	Sr	Pm	So	Sm	Pr	Po	Sm	Sr	Pm	So	Sm	Pr
KGa-1b*	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	448	—	—	519	—	—	581
KGa-1b^	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	462	—	—	517	—	—	575
KGa-2*	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	437	—	—	506	—	—	553
KGa-2^	<20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	462	—	—	509	—	—	549
SWy-2^	<20	—	—	51	106	115	123	139	165	—	—	—	—	—	—	—	592	622	640	689	—	—	734
SWy-2″	<20	—	—	59	109	119	127	148	164	—	—	—	—	—	—	—	598	612	628	685	—	—	726
SAz-1*	<20	—	—	78	112	136	—	—	175	—	—	—	—	—	—	—	512	—	—	633	—	—	680
SAz-^	<20	—	—	65	72	80	121	144	172	—	—	—	—	—	—	—	546	—	—	639	—	—	691
SAz-1**	<20	—	—	64	70	76	117	146	174	—	—	—	—	—	—	—	542	—	—	633	—	—	689
STx-1*	<20	—	—	82	—	—	—	—	122	126	—	—	150	—	—	173	457	503	553	669	—	—	722
STx-1^	<20	—	—	69	—	—	—	—	113	122	—	—	146	—	—	169	595	—	—	679	—	—	719
STx-1^	<20			51	—	—	—	—	89	104	—	—	130	—	—	153	451	485	547	663	—	—	712
Syn-1^	<20	—	—	37	—	—	—	—	84	—	—	—	—	—	—	—	378	441	473	494	554	600	669
Syn-1″	<20	—	—	33	52	61	—	—	85	—	—	—	—	—	—	—	366	—	—	483	544	602	666
SHCa-1^	<20	—	—	64	—	—	—	—	85	—	—	—	—	—	—	—	617	—	—	636	—	—	663
SHCa-1″	<20	—	—	54	—	—	—	—	78	—	—	—	—	—	—	—	528	—	—	617	—	—	711
PFl-1*	<20	—	—	93	—	—	—	—	128	163	—	—	215	—	—	260	311	—	—	441	—	—	530
PFl-1^	<20	43	57	81	113	130	—	—	146	169	199	207	220	237	250	270	344	—	—	442	—	—	527
PFl-1″	<20	43	52	67	114	120	—	—	128	150	—	—	196	—	—	225	305	—	—	444	—	—	538

DTA analysis

Sample	Dehydration												Dehydroxylation							Melting			Recrystallization				
	Peak (1)									Peak (2)																	
	Po	Sm	Sr	Pm	So1	Sm1	So2	Sm2	Pr	Po	Pm	Pr	Po	Sm	Sr	Pm	So	Sm	Pr	Po	Pm	Pr	Po	Pm	So	Sm	Pr
KGa-1b*	—	—	—	—	—	—	—	—	—	—	—	—	483	—	—	575	—	—	618	—	—	—	974	990	—	—	994
KGa-1b^	—	—	—	—	—	—	—	—	—	—	—	—	452	—	—	518	—	—	577	—	—	—	980	993	—	—	997
KGa-2*	—	—	—	—	—	—	—	—	—	—	—	—	474	—	—	568	—	—	604	—	—	—	961	977	—	—	981
KGa-2^	—	—	—	—	—	—	—	—	—	—	—	—	439	—	—	513	—	—	557	—	—	—	965	984	—	—	994
SWy-2*	90	—	—	135	—	—	170	185	209	234	332	374	601	—	—	684	—	—	737	—	—	—	889	923	948	960	976
SAz-1*	<70	—	—	178	204	228	269	327	368	—	—	—	548	—	—	641	695	704	721	815	854	883	950	979	992	1013	1106
STx-1*	<70	—	—	167	198	217	249	327	351	—	—	—	593	—	—	681	—	—	730	829	894	931	982	1008	1023	1080	1106
Syn-1*	90	—	—	139	—	—	—	—	188	251	319	353	392	458	502	532	563	578	673	—	—	—	939	990	—	—	1009
SHCa-1*	<70	—	—	156	—	—	200	250	265	265	331	360	727	741	758	827	—	—	888	1122	1175	1196	—	—	—	—	—
PFL-1*	97	—	—	152	—	—	—	—	196	209	272	307	377	—	—	455	—	—	526	—	—	—	850	872	—	—	915

2.7.3 Exchange Capacity Analysis

Clay minerals have the property of absorbing certain ions and retaining them in an exchangeable state. The most common exchangeable cations, in order of usual relative abundance, are Ca^{2+}, Mg^{2+}, H^{+}, K^{+}, NH_4^{+}, Na^{+} (Grim, 1968). As was stated before, it is commonly believed that cation exchange occurs due to the broken bonds around the crystal edges, the substitutions within the lattice, and the hydrogen of exposed surface hydroxyls that may be exchanged. In addition, the negative charge caused by substitutions within the lattice structure is permanent and pH independent, whereas the charges on the edges and the exposed hydroxyls surface depend upon pH.

The basal siloxane surfaces of kaolinite are believed by many researchers (van Olphen, 1977; McBride, 1976; Rand and Melton, 1977; Williams and Williams, 1978) to carry a constant structural charge due to the isomorphous substitution of Si^{4+} by Al^{3+}, whereas the charge on the edges is due to the protonation/deprotonation of exposed hydroxyl groups and therefore depends on the solution pH. Although the CEC of edges and the basal surface hydroxyl plane is strongly pH-dependent, however, concentration of an exchange cation strongly influences the pH effect during CEC measurement. For example, in the case of edge CEC, assuming A^{+} is the index cation, the following reactions take place (Ma and Eggleton, 1999):

$$\text{Si-OH} = \text{Si-O}^{-} + \text{H}^{+}$$

$$\text{Si-O}^{-} + \text{A}^{+} = \text{Si-O-A} \qquad (2.12)$$

$$\text{Si-OH} + \text{A}^{+} = \text{Si-O-A} + \text{H}^{+}$$

An increase in the $[A^{+}]$ concentration will push the exchange reaction towards the right and decrease Si-OH on the broken edges, giving rise to a higher CEC value. On the other hand, when $[OH^{-}]$ concentration increases, negative charges are developed at the edges of the particles. Therefore, under acidic conditions, the CEC of edges and basal surface hydroxyl planes can still contribute most to the total

CEC, whereas the total CEC is lower since some exchangeable sites are occupied by hydrogen. Hence, cation exchange sites on the edges of kaolinite crystals and other phyllosilicate plates can not simply be considered to be completely inactive in the acidic range of pH. In other words, the kaolinite CEC measured under strongly acidic conditions may not derive from substitutions, but rather from broken edges and possible exposed (OH) planes.

2.7.4 Molecular Characterization

2.7.4.1 FTIR Studies

Infrared (IR) spectroscopy has a long and successful history as a complementary method to X-ray diffraction (XRD) and other methods used to investigate clays (McKelvy *et al*., 1996 and Stuart, 1996). An IR spectrum can serve as a fingerprint for mineral identification, but it can also give unique information about the mineral structure, including the family of minerals to which the specimen belongs and the degree of regularity within the structure, the nature of isomorphic substituents, the distinction of molecular water from constitutional hydroxyl, and the presence of both crystalline and non-crystalline impurities (Farmer, 1979). In Figure 2.20 and Table 2.5, the IR spectra of more common clay minerals, i.e., kaolinite (KGa) and Wyoming montmorillonite (SWy) and their interpretation are shown respectively.

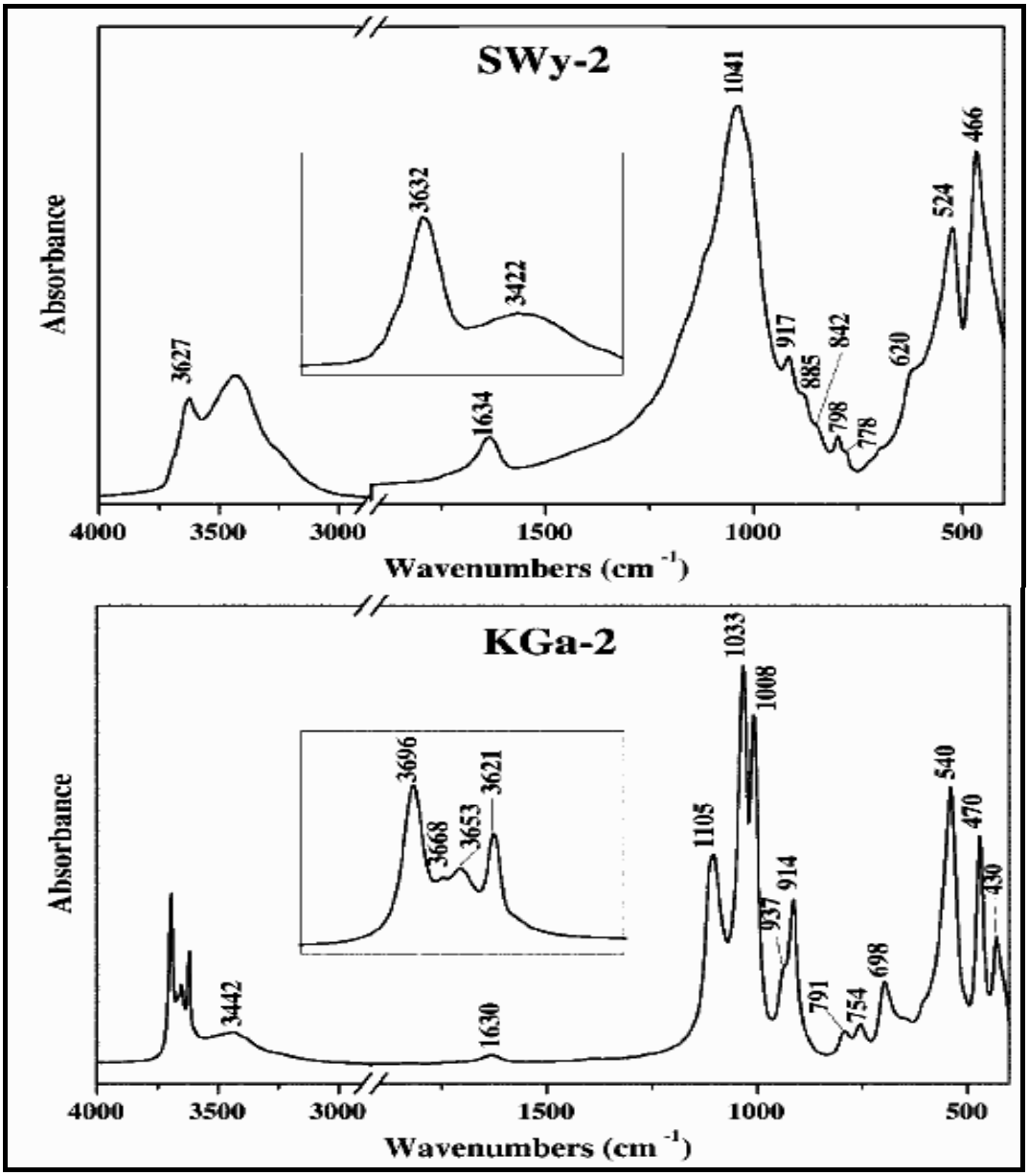


Figure 2.20 IR spectra of montmorillonite (SWy-2) and kaolinite (KGa-2) using KBr pellet (Madejova and Komadel, 2001)

Table 2.5 : IR bands of kaolinite (KGa) and montmorillonite (SWy) clay along with their assignments (Madejova and Komadel, 2001)

KGa-1b			KGa-2	
KBr	ATR	Assignment	KBr	ATR
Position (cm^{-1})			Position (cm^{-1})	
3694	3689	OH stretching of inner-surface hydroxyl groups[1]	3696	3691
3669	3669	OH stretching of inner-surface hydroxyl groups[2]	3668	—
3653	3651	OH stretching of inner-surface hydroxyl groups[2]	3653	3650
3620	3619	OH stretching of inner hydroxyl groups	3621	3619
3457	—	OH stretching of water	3442	—
1635	—	OH deformation of water	1630	—
—	1115	Si–O stretching (longitudinal mode)	—	1114
1102	—	perpendicular Si–O stretching	1105	—
1033	1027	in-plane Si–O stretching	1033	1028
1011	1005	in-plane Si–O stretching	1008	1004
938	937	OH deformation of inner-surface hydroxyl group	937	935
915	912	OH deformation of inner hydroxyl groups	914	912
791	788	Si–O	791	789
755	751	Si–O, perpendicular	754	750
697	681	Si–O, perpendicular	698	684
—	645	Si–O	—	641
541	—	Al–O–Si deformation	540	—
472	—	Si–O–Si deformation	470	—
432	—	Si–O deformation	430	—

SWy-2		
KBr	ATR	Assignment
Position (cm^{-1})		
3632[1]	—	OH stretching of structural hydroxyl groups
3627	3626	OH stretching of structural hydroxyl groups
3422[1]	3393	OH stretching of water
1634	1632	OH deformation of water
—	1116	Si–O stretching (longitudinal mode)
1041	1003	Si–O stretching
917	916	AlAlOH deformation
885	885	AlFeOH deformation
842	846	AlMgOH deformation
798	797	Si–O stretching of quartz and silica
778	779	Si–O stretching of quartz
	687	Si–O
620	623	Coupled Al–O and Si–O, out-of-plane
524	—	Al–O–Si deformation
466	—	Si–O–Si deformation

2.7.4.2 NMR Studies

The Nuclear Magnetic Resonance (NMR) phenomenon is based on the transition of the nuclear spin from low to high energy spin level. Once the spectrum is obtained, it can provide useful information regarding the amount of nuclei and the chemical environment of the nucleus generating the signal.

High-resolution ^{29}Si and ^{27}Al MAS NMR spectroscopy has been found to be applicable to the study of clay minerals. The ^{29}Si MAS spectroscopy gives significant information as for the variation of the chemical environment of silicon atoms, monitoring and distinguishing between the microcrystalline and the amorphous phases. On the other hand, the ^{27}Al NMR spectroscopy can provide useful information regarding the distribution of aluminum atoms in the tetrahedral and the octahedral layer of minerals such as montmorillonite.

The fundamental structural unit of the silicate minerals is a silicon atom surrounded by four tetrahedrally oriented oxygen atoms. The different organizations of the tetrahedral in mono-, bi-, or tri-dimensional structures can be detected with the MAS ^{29}Si spectroscopy, as they give rise to different signals resonating in well-defined chemical shift intervals. More precisely, the spectroscopy allows determining the number of the Si–O–Si bridges for silicon atom. With four bridges, the structure extends to three dimensions, as in the case of quartz or cristobalite. This structural unit is named Q_4. With three bridges the tetrahedral form two-dimensional layers, as in the case of phyllosilicates such as kaolinite and montmorillonite. The structure is named Q_3. A mono-dimensional chain is characterized by only two Si–O–Si bridges for silicon atom, and is indicated as Q_2. The single Si–O–Si bridge, which is indicated as Q_1, characterizes the terminal group of a mono-dimensional chain. The Q_0 term designates the single isolated tetrahedron, lacking any bond with other groups. The structural units of the Q_4, Q_3, Q_2, Q_1 and Q_0 groups are shown in Figure 2.21, together with the typical ^{29}Si resonance intervals.

It should be mention that, there have been several other studies using solid-state NMR of nuclei such as ^{7}Li, ^{23}Na, ^{113}Cd and ^{133}Cs adsorbed onto clays (Chu *et al*., 1987; Bank *et al*., 1989; Laperche *et al*., 1990; Liang and Sherriff, 1993; Weiss *et al*., 1990; Tinet *et al*., 1991). These studies also base all structural assignments on chemical shift and line-shape information.

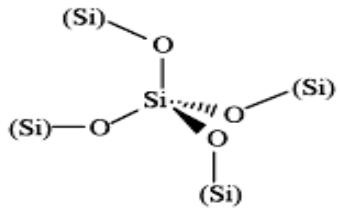
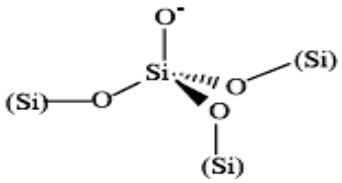
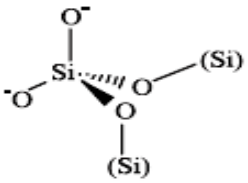
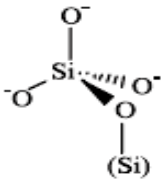
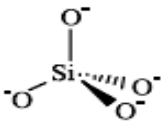
	Structural Unit	^{29}Si Resonance Interval (ppm)	
		crystalline	amorphous
Q_4		107-111	
Q_3		93-101	99-102
Q_2		82-91	80-85
Q_1		77-82	
Q_0		66-72	

Figure 2.21 Structural units and ^{29}Si resonance intervals (Zendri *et al*., 2004)

Analyses by solid state NMR spectroscopy can be applied directly on treated samples in order to study the nature of soil-stabilizer reactions. For instance, several investigations have been undertaken in order to assess the chemical properties and the adhesive interactions between lime and brick fragments (Mayer and Baronio, 1997). As a matter of fact, these studies have demonstrated that the interaction between the brick surface and calcium hydroxide is chemical, with the formation of new composites. Zendri *et al.* (2004) studied the interaction between clay and lime mixtures by using ^{29}Si MAS spectroscopy. Based on the results the following conclusions were made.

a) The tri-dimensional silicates (Q_4) are not attacked by lime.

b) The attack occurs on the bi-dimensional clay minerals (Q_3), with the degree of degradation being poor in the crystalline clay structures (Q_{3cr}), and more efficient on clay structures that are in the amorphous state (Q_{3am}). Thus, in the phyllosilicates that were present exclusively in the crystalline form, the 5 months action of lime brought about only a scantly detectable conversion into linear Q_2 structure.

c) With the aid of the ^{29}Si MAS NMR spectroscopy, a real chemical interaction between lime and clay was detected. This reaction is illustrated in Figure 2.22.

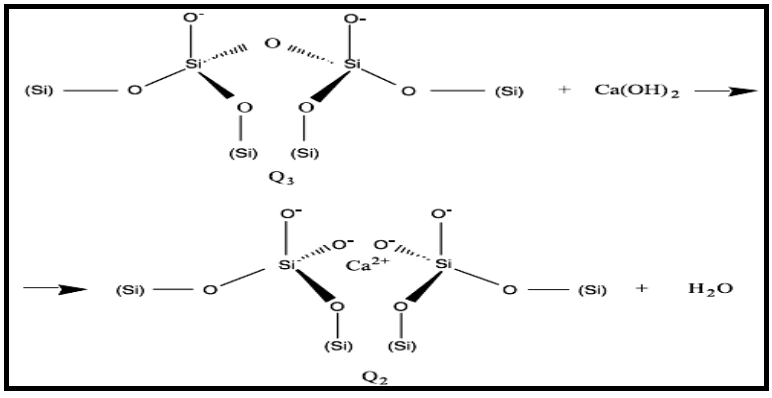


Figure 2.22 Chemical interaction between lime and clay (Zendri *et al*., 2004)

2.7.5 Leaching Characterization

Extraction test on stabilized soil is performed by placing a leachant such as water in contact with the treated material for a specific duration of time. At the end of the test, a sample of supernatant is removed and chemically analyzed to determine the soluble elemental fraction.

In order to provide the best data relating to the actual leachability of stabilized soil at a specific site, in-situ measurements could be considered the most complete representation. However, this would have to occur over large time-scales to account for changes in the environmental conditions such as temperature, rainfall, and etc. On the other hand, these conditions could vary considerably in the long-term and the initial assessment cannot occur indefinitely. For this reason, many testing approaches attempt to emulate the long-term behavior by exaggerating conditions in the short-term (aggressive tests). Most extraction tests can be classified into one of the following categories:

a) agitated extraction test

b) non-agitated extraction test

c) sequential extraction test

d) concentration build-up test

Agitated extraction test is based on achieving equilibrium as quickly as possible by mixing the stabilized material with the leachant. Equilibrium conditions can be considered to have occurred when the total dissolved solids (elements) reaches a steady state condition. This can be assessed indirectly via monitoring pH, as this is a measure of H^+ ion concentration. The method of mixing samples is also important since it determines the level of particle abrasion. Various mixing techniques and number of agitated leaching tests currently being used are shown in Figure 2.23 and Table 2.6, respectively.

Many tests require leachant to simulate rain. Carbon dioxide saturated distilled water can be used for this purpose. This is relatively simple to produce by allowing the distilled water to equilibrate overnight with air, producing water with a pH of 5.6. The quantity of elements or compounds found in the resultant solution depends on how much available soluble material is present and upon final equilibrium conditions. However, it is important to keep solid to liquid ratio high enough to avoid over dilution of important elements to the point where they are below the detection limits of analytical equipment. High ratios also have the potential to limit the effects of sampling errors.

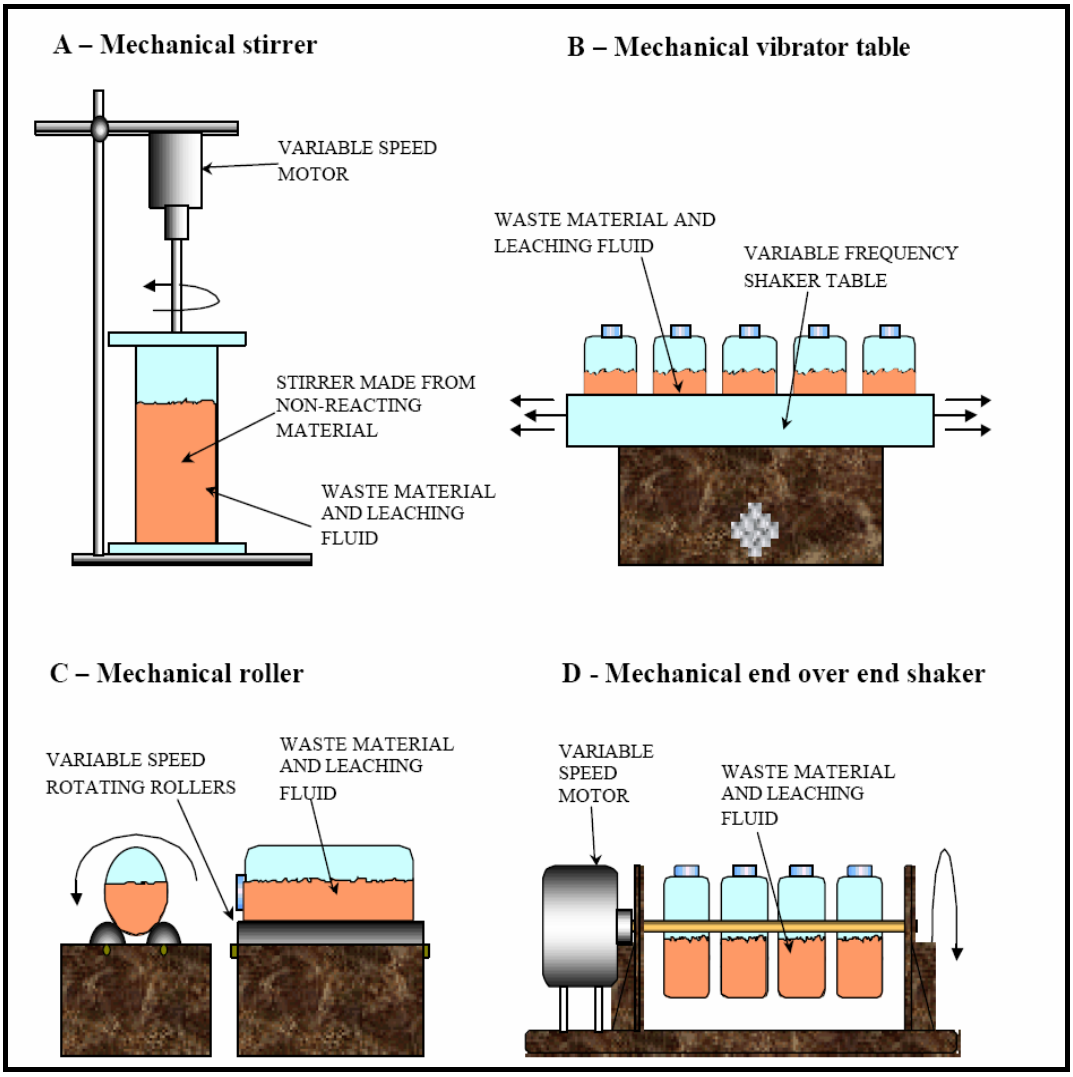


Figure 2.23 Mixing methods for extraction tests (Boardman, 1999)

Table 2.6 : Agitated leaching tests currently being used (Boardman, 1999)

Test name	Development status	Leaching container	Sample preparation	Sample mass	Leachant	Solid to liquid ratio	Agitation method	Duration of test	Method of leachate separation
Waste Extraction Test (WET), California	Regulatory method (SOC, 1985)	Polyethylene or glass container	Milling 0.45m m filtration	50g	0.2M sodium citrate at pH 5.0	1:10	Shaker table or rotary method	48h	Centrifugation, 0.45m m filtration
Toxicity Characteristics Leaching Procedure (TCLP, U.S. EPA 1311)	Standard method (U.S. EPA, 1986)	Any material compatible with sample, zero headspace extractor (ZHE) for volatiles	Cutting/crushing and grinding. Solid/liquid phase separation. No structural integrity	100g 25g for ZHE	Buffered acetic acid 1)pH=4.93 2)pH=2.88	1:20	End over end (30rpm)	18h	0.6 to 0.9 m m borosilicate glass fibre filter combines liquid phase with extract
Equilibrium Extraction (EE), Environment Canada.	Published research method (EC, 1990)	Inorganic: 250ml wide neck plastic sample bottle. Organic: 500ml glass	Inorganic: Grinding Organic: Pestle and mortar	Inorganics 40g Organics 80g	Distilled water	1:4	National Bureau of standards rotary extractor	7 days	0.45m m vacuum screen
Multiple Batch Leach Testing (MBLP), Environment Canada	Published research method (Constable and Côté, 1986)	1 to 2 litre Square polyethylene or glass bottle	Remove free liquid. Reduce particle size to <9.5mm	Variable to fill 90% of bottle	Distilled water. Acidic water buffer to pH4.5. Synthetic municipal waste	1:4 or 1:20	Slow rotary tumbling	24h	0.45mm filtration

In recent years, few attempts to understand the leaching characteristics of lime stabilized soils have been made. For instance, Goswami and Mahanta (2007) conducted a series of tests on the leaching characteristics of fly ash and lime stabilized lateritic soils. As can be seen in Table 2.7, the addition of fly ash and lime affects the leaching potentials of the metals. The extent and direction of change depending on the fly ash and lime content of the soil. Based on their findings, the increase in Al concentration is probably due to the dissolution of alumino-silicate minerals as a result of highly alkaline soil pore chemistry created by lime addition. According to McBride (1994), Al solubility in pure water is determined by a sequence of hydrolysis steps that ultimately result in the precipitation of $Al(OH)_3$ at pH above 5, and dissolution of $Al(OH)_3$ as aluminate anion at pH above 8. Furthermore, in an acidic soil environment, the leachability of metals tends to increase and therefore a higher concentration of the metals is present in the aqueous solution. This explains the higher soluble Fe^{3+} level at low pH. A similar increase in Fe, Al and Mg on lime treatment has been reported by Boardman *et al*. (2001). According to Carroll and Starkey (1971), the leaching result of the acid treatment shows that the arrangement of silica and alumina layers in clay minerals influences the removal of silica and alumina. The reactivity of minerals with acid can be shown in the order below:

Montmorillonite > Metabentonite > Kaolinite > Halloysite = Illite (2.13)

Table 2.7 : Aqueous concentrations of various metals for different mix designs (Goswami and Mahanta, 2007)

Mix	Lime (%)	Metal concentrations (mg/L)												
		Cd	Cr	Hg	Fe	Ni	Pb	Zn	Mg	Cu	Mn	Al	Ca	K
BFA	0	0.009	ND	0.0008	ND	0.020	ND	0.162	3.592	ND	0.204	1.304	58.67	8.600
RLS	0	0.010	0.125	0.0005	0.034	0.005	ND	0.298	3.226	ND	0.774	1.710	2.630	6.200
20FA	0	0.004	ND	0.0007	ND	0.009	ND	0.063	2.629	ND	0.010	0.970	ND	5.700
35FA	0	0.008	ND	0.0005	ND	0.005	ND	0.104	3.134	ND	0.280	1.151	11.00	6.000
50FA	0	0.010	ND	0.0004	ND	ND	ND	0.143	3.447	ND	0.737	1.240	17.08	6.700
20FA	2	0.001	ND	ND	0.134	0.029	ND	0.036	9.951	ND	0.665	8.320	456.4	5.700
35FA	2	0.005	ND	ND	0.094	0.030	ND	0.021	10.58	ND	0.530	7.995	406.0	5.700
50FA	2	0.009	ND	ND	0.044	0.037	ND	0.016	11.25	ND	0.445	5.368	389.3	5.900
20FA	4	0.007	ND	ND	0.230	0.094	ND	0.043	12.35	ND	0.621	10.45	538.0	7.800
35FA	4	0.008	ND	ND	0.129	0.091	ND	0.041	12.01	ND	0.511	8.681	559.0	7.500
50FA	4	0.008	ND	ND	0.052	0.088	ND	0.017	12.32	ND	0.389	4.250	768.0	7.400
Allowable Limits	–	0.005	0.050	0.0010	0.300	–	0.050	5	150.0	1.000	–	–	–	–
Threshold Limits	–	0.500	5.000	0.1000	30.00	–	5.000	500	15000	100.0	–	–	–	–

Notes: ND, not detected.

2.8 Physical Analysis of the Stabilized Soil

2.8.1 Compaction Characteristics

The engineering properties of a stabilized soil such as compressive strength, stiffness and compressibility are influenced by several factors including type and proportion of soil, stabilizer and water content, curing conditions, and the moisture and density at which the soil is compacted. A typical moisture density curve is shown in Figure 2.24.

In general, a high level of compaction enhances the most important soil parameters. As demonstrated in Table 2.8, the addition of lime to various soil minerals increases their optimum moisture content (OMC) and decreases their maximum dry density (MDD) for the same compactive effort. The increase in OMC is mainly because of two reasons. First of all, the reaction between lime and soil particles that causes water to be hydrated from the soil and secondly, the subsequent flocculation and agglomeration process. Hence these two reactions increase the affinity of soil for water, leading to an increase in OMC. On the other hand, the formation of coarser aggregates with more disoriented structure as a result of soil flocculation and also the weak cementitious materials that are formed at the early stages of the lime reaction process, would bind the soil particles together, thus offering a greater resistance to compaction and consequently decreasing the MDD for a given compactive effort (Diamond and Kinter, 1965).

A comparative evaluation was conducted by Ghazali (1981) in order to investigate the effect of acidic and basic chemical additives on the maximum dry density and optimum moisture content of soils containing different percentages of kaolin clay. Based on the results, in contrast to alkali treated soils, the addition of phosphoric acid to clayey soils caused a sharp decrease in OMC with higher reduction being observed for further addition of the acid. Ghazali (1981) suggested that there were two reasons responsible for this type of behavior. First the existence and lubrication behavior of phosphoric acid and secondly, the water release due to

the reaction of phosphoric acid with the aluminum sheet in the soil medium. This is consistent with Demirel *et al*. (1962) findings who have also reported an inverse relationship between optimum moisture content and phosphoric acid content. On the other hand, the maximum dry density also follows a different trend in comparison to alkali treated soils. It is apparent that, the MDD of acid treated soils has a noticeable increase as high as two fold. According to Ghazali (1981), this is due to the formation of amorphous aluminum phosphate cementing gel which has a higher specific gravity than the alumina sheet.

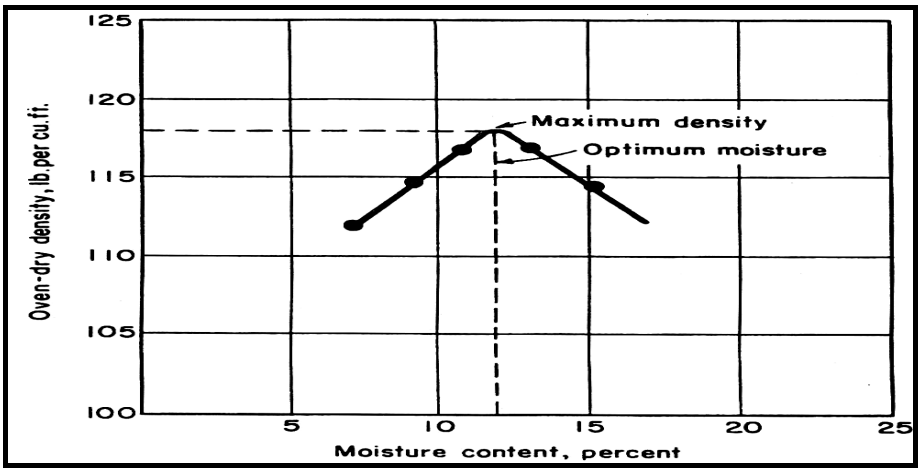


Figure 2.24 Typical moisture-density curve

Table 2.8 : Compaction characteristics of soil minerals prior and after lime treatment (Bell, 1996)

Material	Optimum lime content (%)	Optimum moisture content (%)	Maximum dry density (Mg/m^3)
Kaolinite	0	29	1.4
	6	31	1.33
Montmorillonite	0	20	1.29
	4	25	1.15
Quartz	0	28	1.41
	6	32	1.40

2.8.2 Compressive Strength

The strength gain for stabilized soils is often quoted in terms of unconfined compression strength (UCS). It has been confirmed by many researchers that lime treatment enhances the strength of the natural soil with the rate of improvement being dependent on the amount of pozzolans present (Balasubramaniam *et al*., 1989; Locat *et al*., 1990; Bell, 1996; Narasimha Rao and Rajasekaran, 1996).

Laboratory investigations carried out by Bell (1996) on the strength characteristics of different soil minerals indicated that expansive clay minerals such as montmorillonite respond more quickly to strength development in comparison to non-expansive clay minerals. Also it was found that, the addition of small amount of lime to kaolinite and quartz would boost their compressive strength even at the early stages of curing (Figure 2.25). This is in good agreement with the results recorded by Balasubramaniam *et al*. (1989) who indicated that with a 28 day curing period, the strength of all lime treated samples showed an increase of approximately 4 to 5 times of the natural soil. This would add evidence to the conclusion that the stabilization reactions have been substantially occurring in these samples. Furthermore, based on Wild *et al*. (1989) findings, as the degree of interlocking of soil particles increases during curing, larger forces are required to overcome their bonding and to break up the particles.

The increase in strength of phosphoric acid stabilized soils has been reported by many researchers (Lyons and McEwan, 1962; Sutton and McAlexander, 1987; Medina and Guida, 1995). Figure 2.26 demonstrates the results collected from the UCS test performed on untreated and treated clayey soils with different percentages of phosphoric acid. As can be seen, phosphoric acid treatment increased the strength characteristics of the compacted soil. Based on Demirel *et al.* (1962) observations the unconfined compressive strength of treated soils had a considerable rise with increasing acid content. Furthermore, for each combination of phosphoric acid and soil there appears to be a curing time beyond which there will be no further strength development.

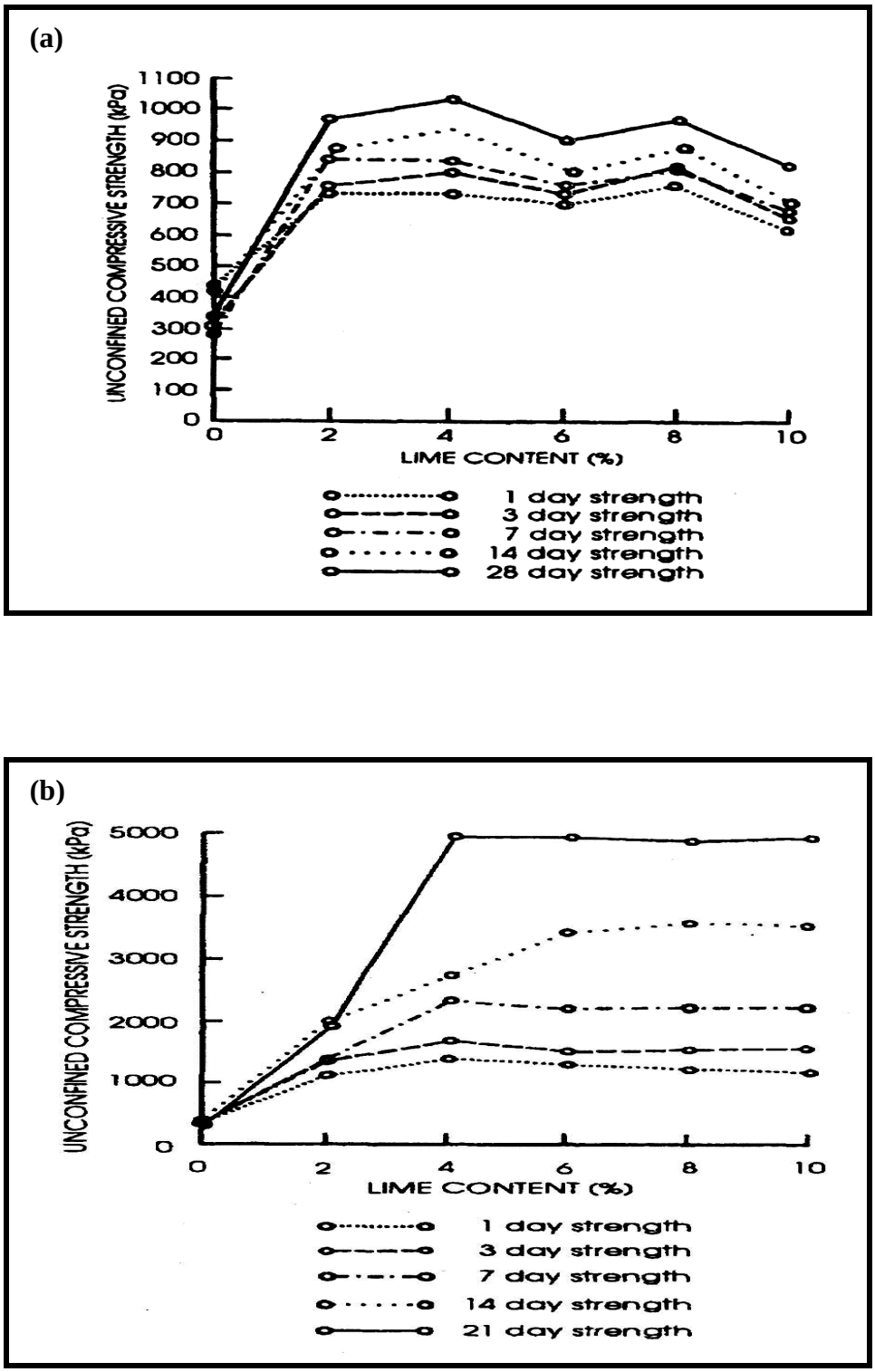


Figure 2.25 Unconfined compressive strength of (a) kaolinite and (b) quartz with different lime content (Bell, 1996)

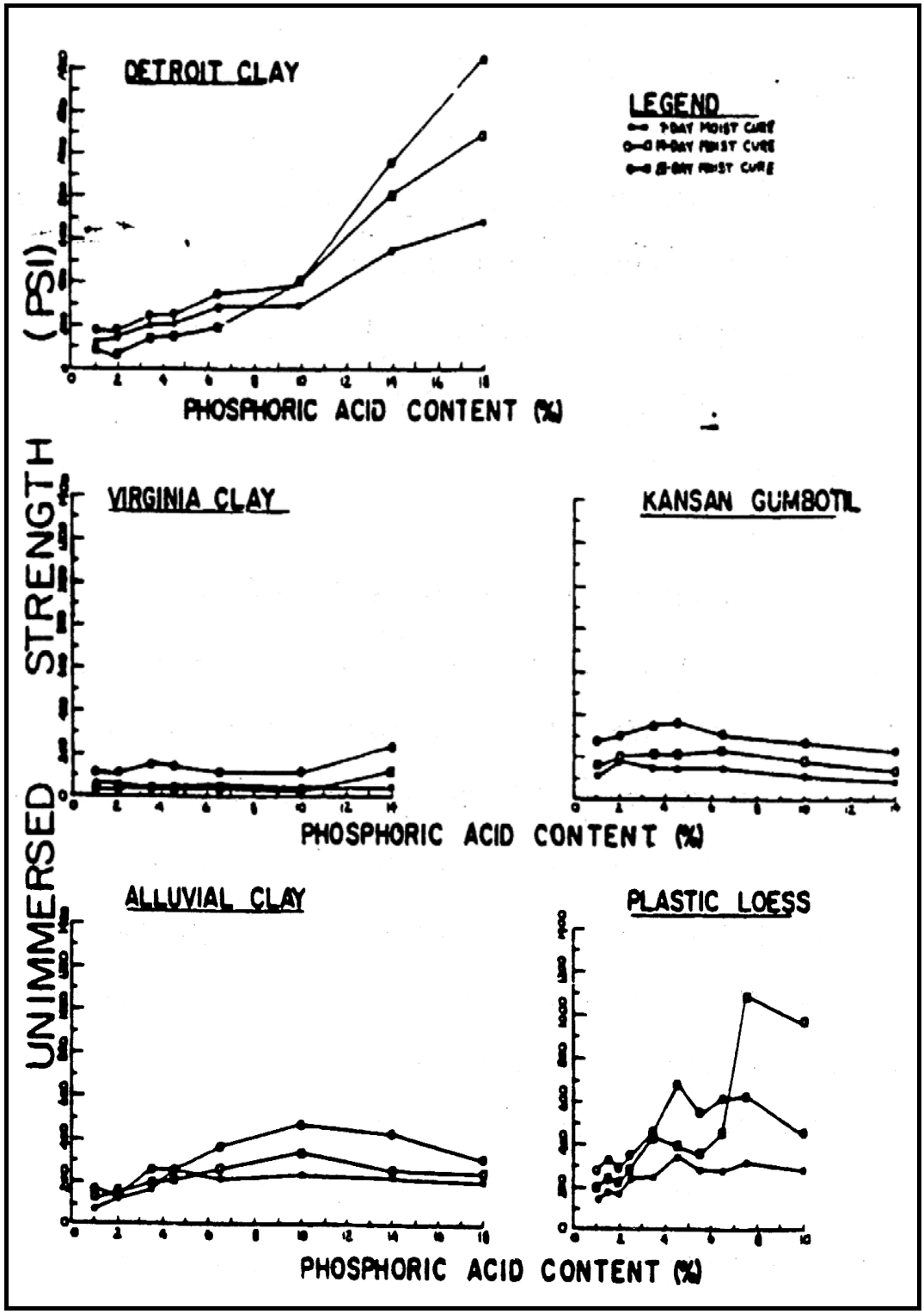


Figure 2.26 Effect of phosphoric acid on the unconfined compressive strength of treated soils (Demirel *et al*., 1962)

2.8.3 Surface Area and Pore Size Distribution

The specific surface area and pore structure of a compacted clay system are undoubtedly two of its most important characteristics in determining both its chemical and physical interactions with its surroundings. This is due to the fact that most of the chemical reactions in soils take place at the surface of the particles. Similarly the interpretation of physical properties such as permeability requires an accurate measurement of specific surface area and knowledge of the pore structure (Mitchell and Soga, 2005). As illustrated in Figure 2.27, there are different types of pores present in soil structure. Information on these pores can be obtained by volumetric determination techniques such as mercury microporosimetry (MM) or from SEM and TEM analysis of thin sections of soil sample.

Mercury microporosimetry test conducted on lime treated marine clays are shown in Figure 2.28. It is evident that there are two families of pores present in soil structure, the intra-aggregate and the inter-aggregate porosities. As can be seen, the lime stabilization process modifies the porous network by lowering the number of large pores to the benefit of smaller ones without causing significant changes in the total pore volume of the soil. As suggested by Choquette *et al*. (1987), this phenomenon can only be explained by plugging of the larger pores by the new formed lamellar and reticular minerals. Moreover, these phases and especially the ones with a reticular texture present a very small porous network which contributes to the increase of smaller pores. Arabi and Wild (1986) have also reported similar pores evolution pattern for lime treated red marl soil. Based on their observation, the continuous formation of cementitious gels would produce considerable changes in pore size distribution of soil fabric towards much finer pores. Hence compensating for the increase in porosity resulted from flocculation of the soil matrix by filling and blocking some of the coarser pores.

The specific surface area (SSA) developed by soil minerals is related to many other soil properties such as ion exchange capacity, reactivity, and etc. The measurement of this property has received much attention in the past. The BET surface area values for various minerals are presented in Table 2.9.

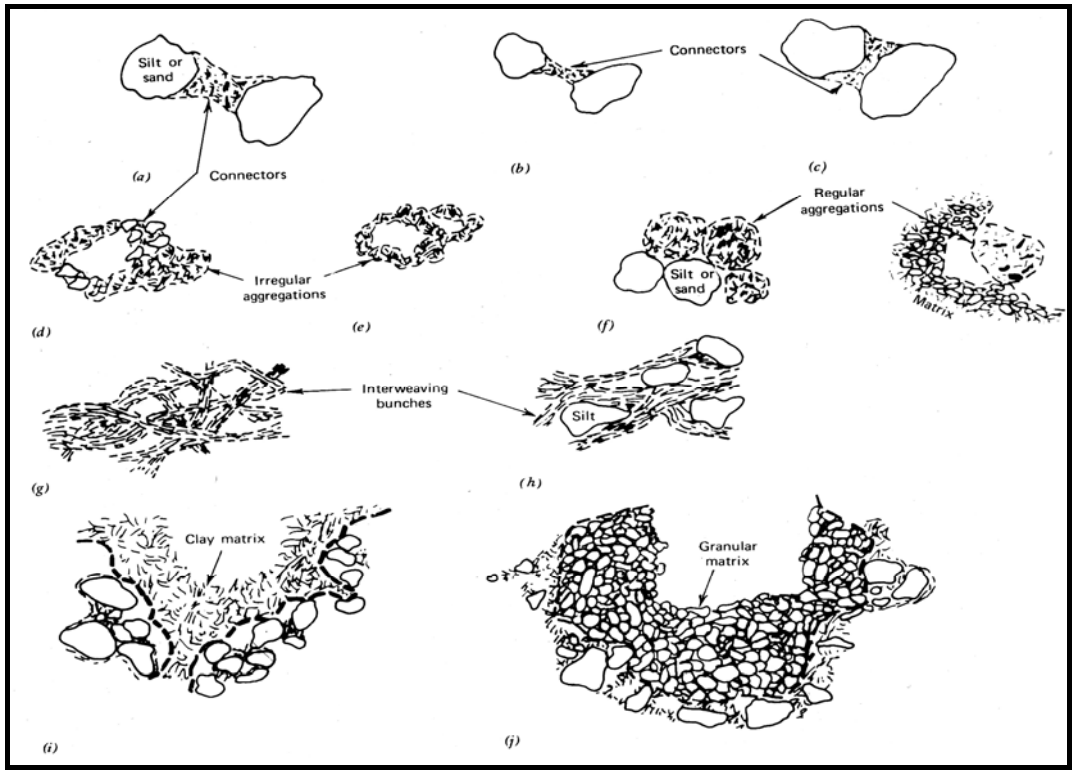


Figure 2.27 Various pores observed in micro-fabric of Tucson silty clay (Mitchell and Soga, 2005)

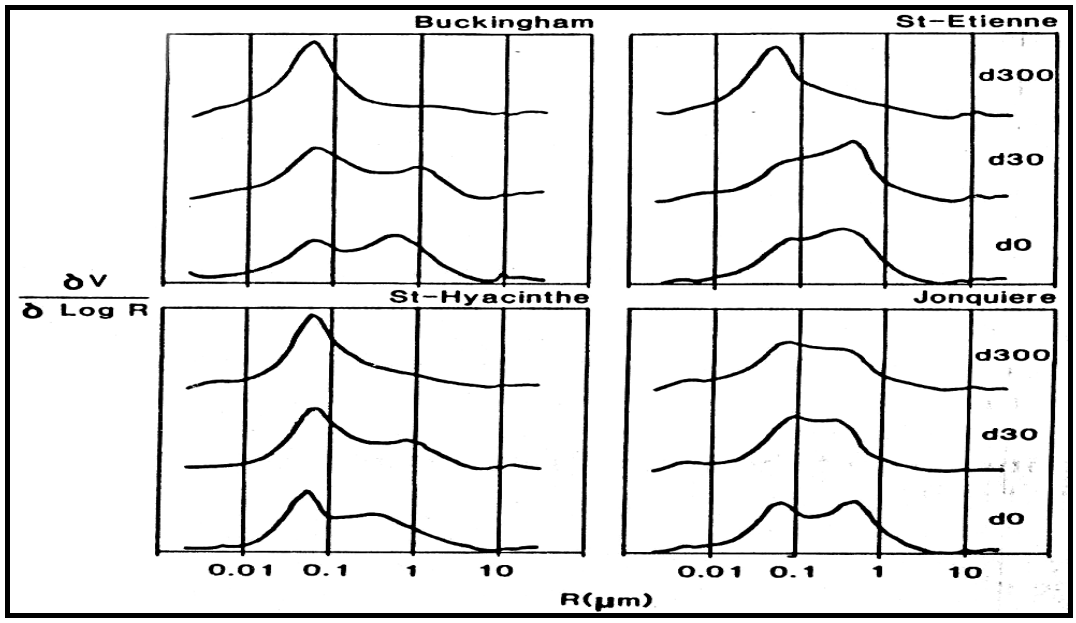


Figure 2.28 Mercury intrusion proximity and its derivative plots in lime treated soils (Choquette *et al*., 1987)

Table 2.9 : BET surface area values of various minerals (Aylmore, 1974)

	Surface area ($m^2 g^{-1}$)					
	BET				$(V-n)$	
Gas	N_2	A	CO_2	Kr	N_2	CO_2
Molecular area $(Å)^2$	16·2	14·1	22·1	19·5	16·2	22·1
Clay						
Sodium A.P.I.–5 Kaolinite	23·1	17·6	12·1	22·2	25·3	20·8
Caesium A.P.I.–5 Kaolinite	22·7	17·6	21·7		24·8	22·8
Calcium A.P.I.–5 Kaolinite	18·9	16·9	13·5		21·6	18·1
Lanthanum A.P.I.–5 Kaolinite	20·7	18·3	12·9		23·5	18·1
Sodium Fithian Illite	95·6	86·8	95·6	123	103	
Caesium Fithian Illite	97·2	87·4	104·4		107	94·6
Calcium Fithian Illite	96·8	89·2	94·3		103	94·9
Lanthanum Fithian Illite	87·2	87·7	86·4		101	92·5
Sodium Willalooka Illite	185		183	200	187	185
Goethite	39·2	35·9	56·3	42·0	43·8	30·4
Hematite	18·0	14·4	25·2	13·8	19·8	16·1
Gibbsite	35·2	29·5	40·9	39·3	42·0	21·7

The tendency of all solid surfaces to attract surrounding gas molecules gives rise to a process called gas sorption. Physisorption is the most common type of adsorption. Physisorbed molecules are fairly free to move around the surface of the sample. As more gas molecules are introduced into the system, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface. Based on the BET theory, one can estimate the number of molecules (N_m) required to cover the adsorbent surface with a monolayer of adsorbed molecules (Figure 2.29). Multiplying N_m by the cross sectional area of an adsorbate molecule yields the sample's surface area.

According to the study carried out by Rodrigues (2003) on smectite clays, it was found that after the acid treatment the BET surface area values of the treated soil showed a significant increase. This was consistent with Tao Yang *et al*. (2006) findings. Based on their results at the early stage of the acid attack, partial degradation of the octahedral layer and the substitution of Na^+ and Ca^{2+} with the H^+

gave rise to a material with lower surface area properties. However, with further acid treatment a gradual increase in the surface area due to the more extensive degradation of the octahedral layer was observed.

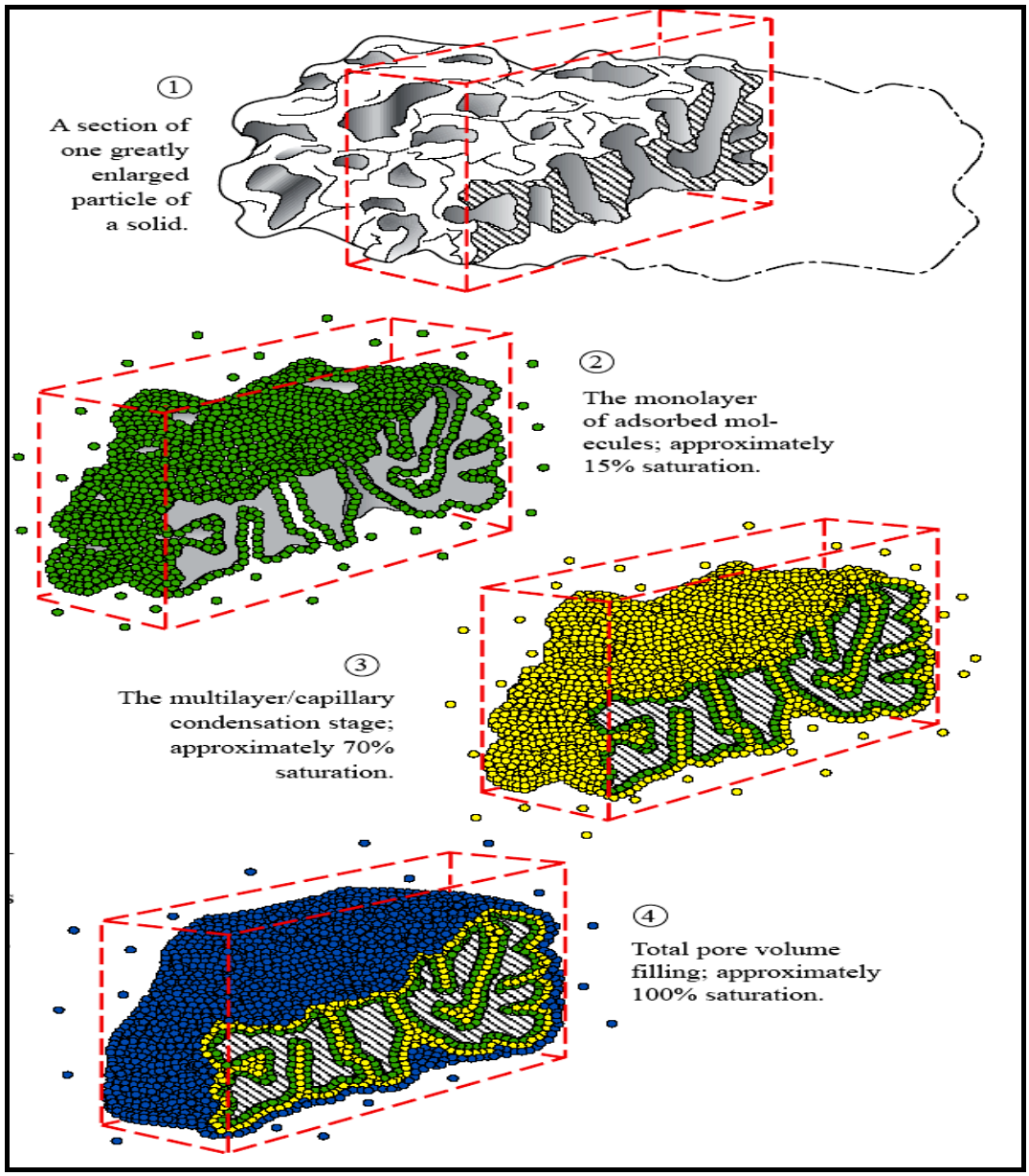


Figure 2.29 Adsorption of gas molecules on solid particles (Quantachrome manual, 2007)

2.9 Summary

This chapter reported the current scientific understanding of soil stabilization. Based on these studies, the efficiency of chemical stabilization in improving the engineering properties of soil depends strongly on the nature of soil-chemical reactions. In the published literatures, a clear lack of understanding regarding determination of appropriate chemical testing methods for assessment of lime treated clayey soils was clearly apparent. Furthermore, it was evident that there is rarely an attempt to understand the mechanisms of acidic stabilizers interactions. These findings formed the basis for selecting the most appropriate methods of analysis.

This research was carried out in an effort to identify various processes controlling the stabilization mechanisms in a low and high pH environment and also to obtain direct structural information on the reaction products.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

To establish a clear understanding of the chemical changes induced by stabilizers on the surface and interlayer of clay particles in order to clearly delineate the possible mechanisms by which clayey soils are modified in a highly acidic and basic environment, it was essential to characterize the soil prior and after treatment. In addition, determining the main physical properties of the soil was important, since they were used to evaluate the relative effects of additives on the engineering properties of the natural soil. Hence based on the main objectives of the thesis, a clear framework of the experiments to be carried out was prepared (Figure 3.1). This provided a well defined and logical progression of the research. Furthermore, it ensured the completion of the project within the restricted time-scale.

It should be noted that since Malaysia has not yet established any standard specification for soil stabilization that suits its local climatic conditions, the procedures implemented in other countries and in particular British Standard (BS) was used throughout this investigation.

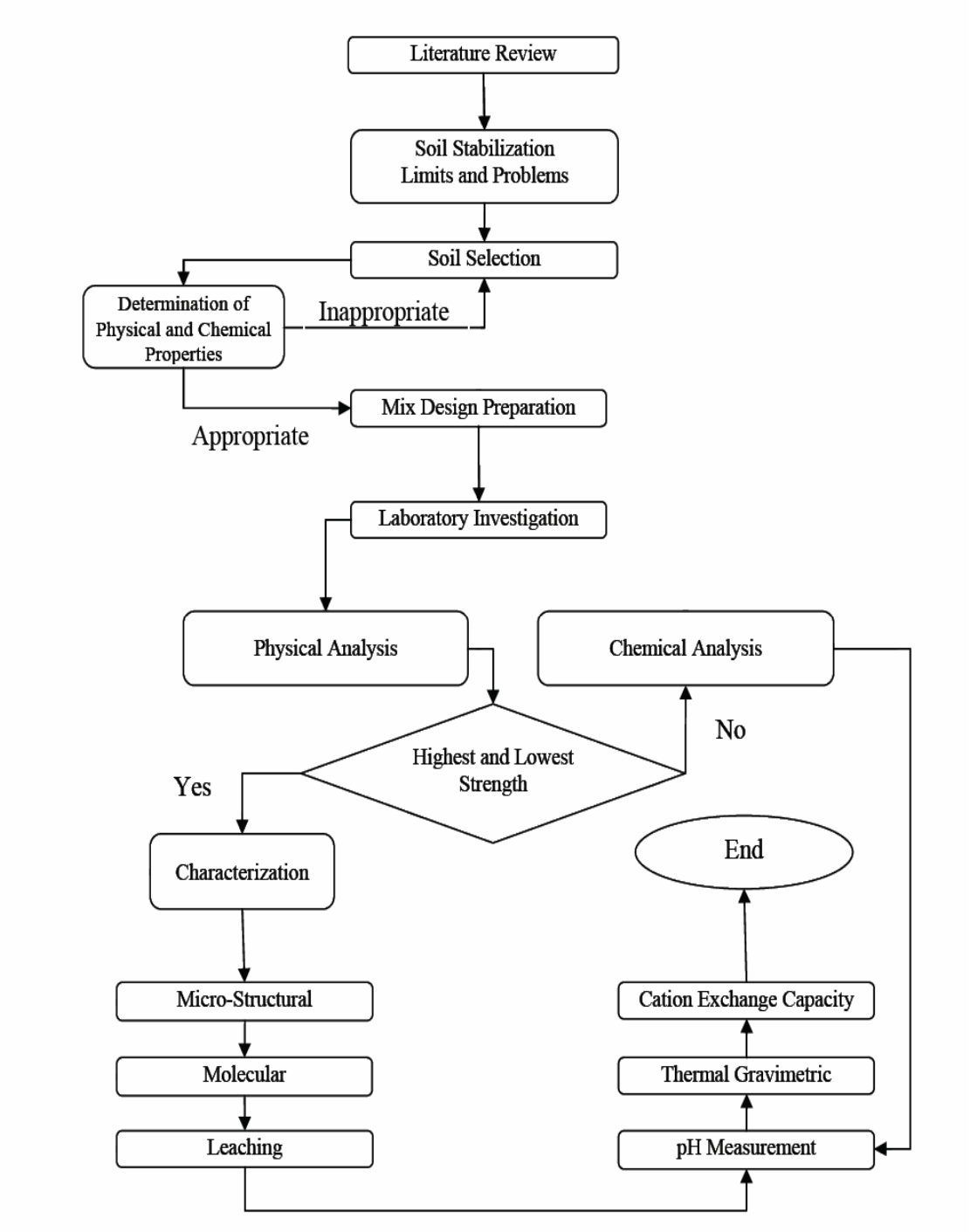


Figure 3.1 Flow chart of research methodology

3.2 Material Specification

3.2.1 Clay Soils

Four soil types formed under different environmental conditions were selected for this study. The physical and chemical characteristic for each individual soil is briefly discussed in the following paragraphs.

As was mentioned in the previous chapter, natural soil deposits in addition to the typical clay mineral constituents usually contain some sort of impurities such as salts and organic matter. Hence, in order to reduce the interference of these materials on soil-stabilizer reactions, more pure soil samples are required.

In this research, Green Bentonite (GB) soil comprised mainly of sodium montmorillonite was used for laboratory experiments. The bulk soil which is an odorless, dry, greenish powder was purchased in 50kg bags from Wyoming located in the Western province of United States. The soil has a high expansive nature and forms gel-like masses in the presence of moisture. The engineering properties and chemical composition of untreated sample is presented in Table 3.1.

The second type of clay used for preparation of lime and phosphoric acid mix designs was the slightly acidic White Kaolin sample. The soil was dominated by kaolinite and illite minerals along with minor constituents of quartz. The physical and chemical properties are shown in Table 3.2.

Finally, two native tropical soils were used in this investigation, i.e., the residual lateritic soil (Laterite Clay) and silty clay (Pink Soil). They were excavated from a hillside located in Southern part of Malaysian Peninsular. The physical and chemical characteristics of the natural soil are presented in Tables 3.3 and 3.4, respectively. As can be seen in Figure 3.2, the Laterite Clay sample possesses a reddish brown colour. The more important features of this soil are summarized below:

a) A slightly acidic nature.

b) High amounts of free iron oxides (The main cause of its reddish colour).

c) High specific surface area value.

d) Presence of kaolinite as the dominant clay mineral.

e) The similar proportions of both silicon and aluminum oxides.

3.2.2 Lime and Phosphoric Acid Stabilizers

The lime used throughout the sample preparation was a laboratory grade hydrated lime in powder state (Table 3.5). In order to confirm its quality, the suitability of lime test in accordance with BS 1924: Part 2: 1990 (clause 5.4.6) was carried out. This was achieved by mixing 5g of lime with 100mL CO_2-free distilled water using a magnetic stirrer for one hour. After leaving the suspension for 24hr in an air tight container, its pH value at 25^o Celsius was calculated according to the following equation:

$$pH_{25} = pH_T + 0.03\ (T\text{-}25) \qquad (3.1)$$

After performing the test for at least three times an average pH_{25} value of 12.40 was achieved which satisfied the 12.35 to 12.45 range indicated in the standard. Also to ensure consistent chemical composition, the lime used in this research was stored in a high temperature oven to prevent the gradual agglomeration of particles. On the other hand, the phosphoric acid was a Merck analyzed, 85% H_3PO_4, of specific gravity 1.71. The chemical composition of the acid is shown in Table 3.6.

Table 3.1 : The physical and chemical properties of the natural Green Bentonite

ENGINEERING & PHYSICAL PROPERTIES	VALUES	CHEMICAL COMPOSITION (Oxides)	VALUES (%)
CEC (meq/100 g)	78.79	SiO_2	60.79
pH (L/S = 2.5)	9.03	Al_2O_3	21.20
Specific Gravity	2.64	Fe_2O_3	6.46
External surface area (m^2/g)	26.50	CaO	0.96
Liquid Limit, LL (%)	301.60	MgO	3.26
Plastic Limit, PL (%)	41.80	Na_2O	6.14
Plasticity Index, PI (%)	259.80	CO_2	1.19
IS Classification	CE	Soluble Phosphorus (P)	0.50 ppm
ICL (%)	7.00	Soluble Aluminum (Al)	250 ppm
Maximum dry density (Mg/m^3)	1.27	Soluble Silica (SiO_2)	40 ppm
Optimum moisture content (%)	37.70	Soluble Calcium (Ca)	0.04 ppm
Unconfined compressive strength (kPa)	281.30		

Table 3.2 : The physical and chemical properties of the natural White Kaolin

ENGINEERING & PHYSICAL PROPERTIES	VALUES	CHEMICAL COMPOSITION (Oxides)	VALUES (%)
CEC (meq/100 g)	12.87	SiO_2	48.18
pH (L/S = 2.5)	4.34	Al_2O_3	31.10
Specific Gravity	2.66	Fe_2O_3	1.03
External surface area (m^2/g)	19.87	MgO	0.86
Liquid Limit, LL (%)	42.20	P_2O_5	9.37
Plastic Limit, PL (%)	21.30	K_2O	4.01
Plasticity Index, PI (%)	20.90	SO_3	2.07
IS Classification	CL	CO_2	1.34
ICL (%)	2	Soluble Phosphorus (P)	5.10 ppm
Maximum dry density (Mg/m^3)	1.64	Soluble Aluminum (Al)	5.80 ppm
Optimum moisture content (%)	18.40	Soluble Silica (SiO_2)	4.00 ppm
Unconfined compressive strength (kPa)	134	Soluble Calcium (Ca)	0.40 ppm

Table 3.3 : The physical and chemical properties of the natural Laterite Clay

ENGINEERING & PHYSICAL PROPERTIES	VALUES	CHEMICAL COMPOSITION (Oxides)	VALUES (%)
CEC (meq/100 g)	14.88	SiO_2	21.55
pH (L/S = 2.5)	4.86	Al_2O_3	24.31
Specific Gravity	2.75	Fe_2O_3	29.40
External surface area (m^2/g)	57.89	Na_2O	0.07
Liquid Limit, LL (%)	75.8	K_2O	0.11
Plastic Limit, PL (%)	39.60	P_2O_5	16.71
Plasticity Index, PI (%)	36.20	SO_3	3.98
IS Classification	MH	CO_2	3.65
ICL (%)	5.00	Soluble Phosphorus (P)	0.40 ppm
Maximum dry density (Mg/m^3)	1.33	Soluble Aluminum (Al)	0.05 ppm
Optimum moisture content (%)	34.00	Soluble Silica (SiO_2)	0.10 ppm
Unconfined compressive strength (kPa)	288.10	Soluble Calcium (Ca)	0.10 ppm
Loss of ignition (%)	6.32		

Table 3.4 : The physical and chemical properties of the natural Pink Soil

ENGINEERING & PHYSICAL PROPERTIES	VALUES	CHEMICAL COMPOSITION (Oxides)	VALUES (%)
CEC (meq/100 g)	10.56	SiO_2	39.77
pH (L/S = 2.5)	4.64	Al_2O_3	32.88
Specific Gravity	2.73	P_2O_5	4.83
External surface area (m^2/g)	20.63	K_2O	1.97
Liquid Limit, LL (%)	46.10	SO_3	0.77
Plastic Limit, PL (%)	28.60	CuO	5.68
Plasticity Index, PI (%)	17.50	ZnO	2.16
IS Classification	ML	Soluble Phosphorus (P)	3.50 ppm
ICL (%)	3.00	Soluble Aluminum (Al)	0.60 ppm
Maximum dry density (Mg/m^3)	1.58	Soluble Silica (SiO_2)	4.00 ppm
Optimum moisture content (%)	20.00	Soluble Calcium (Ca)	0.40 ppm
Unconfined compressive strength (kPa)	197.00	CO_2	1.59
Loss of ignition (%)	0.40		

Table 3.5 : Chemical composition of the hydrated lime

CHEMICAL COMPOSITION	VALUES (%)
Calcium Oxide, CaO	74.23
Phosphorus Oxide, P_2O_5	0.08
Magnesium Oxide, MgO	0.74
Calcium Sulphate, $CaSO_4$	0.12
Ferric Oxide, Fe_2O_3	0.17
Aluminium Oxide, Al_2O_3	0.11
Silica, SiO_2	0.14
Loss on Ignition, LOI	24.35

Table 3.6 : Chemical composition of the phosphoric acid

CHEMICAL COMPOSITION	MAXIMUM QUANTITY (ppm)
Chloride (Cl)	2
Fluoride (F)	1
Nitrate (NO_3)	3
Sulphate (SO_4)	20
Calcium (Ca)	20
Copper (Cu)	0.5
Potassium (K)	5
Magnesium (Mg)	5
Sodium (Na)	200
Zinc (Zn)	2
Lead (Pb)	0.5
Insoluble matter	10

Figure 3.2 The image of natural soils used in this research

3.2.3 Water Quality

Dissolved solids in the pore water may alter the soil chemistry and in some circumstances, could affect the observed test results. As is generally recommended for geotechnical testing practice, distilled water was used in all aspects of sample preparation. On the other hand, for leaching test in order to simulate rain and moreover to prevent the introduction of unknown chemical species, carbon dioxide saturated de-ionized water was used. This was relatively simple to produce by allowing the de-ionized water to equilibrate overnight with air, producing water with an average pH of 5.6.

3.3 Laboratory Full-Scale Mix Design Preparation

3.3.1 Lime and Phosphoric Acid Content

The concentration of stabilizer ions has a great impact on the short and long term reactions which are involved in the initial modification and cementation of the treated samples, respectively. Due to simulation of actual field conditions, it was also important to add practical amounts of lime and phosphoric acid to both mix designs. Furthermore, for comparison reasons, similar quantities of additives for each soil type were taken into consideration as well.

The initial consumption of lime (ICL) test was performed according to BS 1924: Part 2: 1990 (clause 5.4.7). The test was developed by Eades and Grim (1966) and is based on the philosophy of adding sufficient lime to satisfy all primary reactions of the soil while sustaining a high pH environment for promoting the pozzolanic reactions (Little, 1995). It should be noted that due to the highly expansive nature of Bentonite soil, the addition of 100mL of water to 20g of soil, as stated in the standard, made it impossible to perform the test. To obtain a solution that its pH can easily be determined it was necessary to carry out the test at much higher solid to liquid ratios. Therefore, the ICL test for Green Bentonite was performed according to the standard but at a different range of solid to liquid ratios, i.e., 20g : 300mL, 20g : 520mL and 20g : 1000mL.

As was stated by Medina and Guida (1995), a concentration range of 1-5% phosphoric acid by weight of the dry soil seems to be sufficient in improving the geotechnical properties of the soil. Hence, based on the previous studies conducted on phosphoric acid stabilization and also the criteria mentioned above, economically-viable amounts of phosphoric acid which can be implemented in engineering projects were selected for preparation of mix designs.

3.3.2 Compaction Characteristics

In road construction works, the main aim of compaction is to maximize soil's density. On the other hand, the addition of a single anion or cation introduced by the stabilizers can also pose a significant impact on the compaction characteristics of the soil. Therefore, it is rational to suggest that soil-stabilizer reactions are affected by the initial compactive effort, since this has direct influence on the particle spacing and the subsequent crystallization process.

In order to determine the compaction characteristics of the natural soil a standard compaction test in accordance with BS 1377: Part 4: 1990 (clause 3.3.4.1) was performed. This was achieved by compacting the soil into a 1L Proctor mould by applying 27 blows of a 2.5kg circular faced (50mm diameter) hammer on each of the three equal layers. This resulted in a compactive effort of 596 kJm^{-3} being applied. Then based on the moisture-density relationship curve obtained for each individual soil, the optimum moisture content (i.e., the water content at which the maximum dry density was achieved) and its corresponding dry density were determined. In Figure 3.3 the equipments used in the compaction of soil are shown.

Figure 3.3 Compaction analysis equipment

3.3.3 Sample Preparation

In the context of this research, bearing in mind the similarity in the fundamentals of soil-chemical reactions for a particular phosphoric acid or lime treated soil type, a varying level of compaction for each phosphoric acid content or lime content and all the associated mix design combinations would have made the interpretation and comparison of the results difficult. Moreover, to ensure that any observed changes and in particular the strength developments were attributable solely to the action of the stabilizers on the soil particles, the possible contributions caused by the variations in water content and compactive effort needed to be eliminated. Therefore, all mix designs for a particular soil type, had the same amount of water and degree of compaction.

With the exception of Laterite Clay samples, the other three soils were first oven dried and used as they were received (not sieved) in the laboratory. However, investigations conducted on the lateritic soil indicated that oven drying significantly changes its plasticity and compaction properties. Therefore, all mix designs for this type of soil were prepared from air-dried soil. The air-dried soil was then broken into smaller sizes and sieved through a 2mm sieve. The sieving was done to ensure that the soil was of uniform grade throughout the experiment.

In this research, a standard and rational step by step protocol was used for preparing various mix designs. First of all, as was stated in the previous section, the required amount of water known as Optimum Moisture Content (OMC) was determined for each individual soil. Secondly, in the case of acid stabilization, the dried soil was directly mixed with the required amount of water and phosphoric acid until a uniform mixture was achieved. However, for lime treated samples, prior to addition of water, the dried soil and lime were first mixed thoroughly. Also according to laboratory trials an additional quantity of water (2% wet of the optimum) was added to all mix designs to take into account the loss due to evaporation. Finally after compacting the soil into thin wall PVC tubes (50 mm diameter × 100 mm length) under constant compactive effort as specified in BS 1924: Part2: 1990 (clause 4.1.5), they were wrapped with thin plastic film and sealed

to the atmosphere with rubber tight lids (Figure 3.4). The samples were then stored in a controlled temperature room (27±2°C) until required for testing at each of the three curing periods, i.e., 1 month, 4 months and 8 months. This procedure is also believed to effectively represent the curing conditions in a compacted roadway subgrade. While the very top of a compacted base material may have free access to air during the curing period, soil just below the surface does not have open ventilation and will remain moist.

It should be stressed that to ensure the accuracy of the results, four samples for each soil mix design and the three curing periods were prepared. This resulted in an overall 350 cylindrical mould specimens. Also in order to effectively present the obtained results, a specimen designation scheme was used. Letters in the specimen designation indicated soil name and type of treatment, respectively (e.g., GB: Green Bentonite, AT: acid treated, LT: lime treated, and M: months).

Figure 3.4 Prepared samples for various laboratory testing

3.4 Sample Characterization

In general, the characterization studies carried out in this thesis can be divided into three main categories, i.e., Micro-Structural, Molecular, and Leaching. Hence, the time-dependent changes induced in soil-stabilizer matrix were monitored using X-ray Diffractometry (XRD), Energy Dispersive X-ray Spectrometry (EDAX), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR), and leaching analysis. In addition, in order to correlate the observed changes with the improved engineering properties, physical analysis (i.e., Unconfined Compressive Strength and BET surface area analysis) were performed on cured samples. These tests along with some complementary experiments such as Cation Exchange Capacity (CEC), Thermal Gravimetric (TG), and pH measurement are discussed comprehensively in the following paragraphs.

3.4.1 Micro-Structural Characterization

3.4.1.1 X-ray Diffraction

The type and amount of clay minerals present in a soil has a great impact on the behavior that soil exhibits when it is exposed to different environmental conditions. Furthermore, as was seen in the literature review, it is the primary factor that affects the suitability and efficiency of the stabilization technique.

As illustrated in equation 3.2, XRD is based on Bragg's law which states that when a x-ray beam strikes a crystal, the angle at which diffraction occurs is dependent on the inter-atomic spacing between the prominent planes (Figure 3.5). Furthermore, the reflected beams must be perpendicular to the planes of atoms responsible for the scattering and are identified as 001 planes for clay materials (Moore, 1997). The intensities of these planes are controlled by the position of atoms and chemical composition.

$$n\lambda = 2d \sin\theta \qquad (3.2)$$

where:

d = distance of interplanar spacing (as function of θ)

n = order of diffraction

θ = critical angle of incidence of the x-ray beam on the crystal plane

λ = wavelength of the x-rays

Thus since the inter-atomic distances are unique to each mineral, the angle of incidence will be distinct for each mineral. It should be noted that the XRD patterns are identified based on the position of a diffraction line response (represented by 2θ) and the relative intensities.

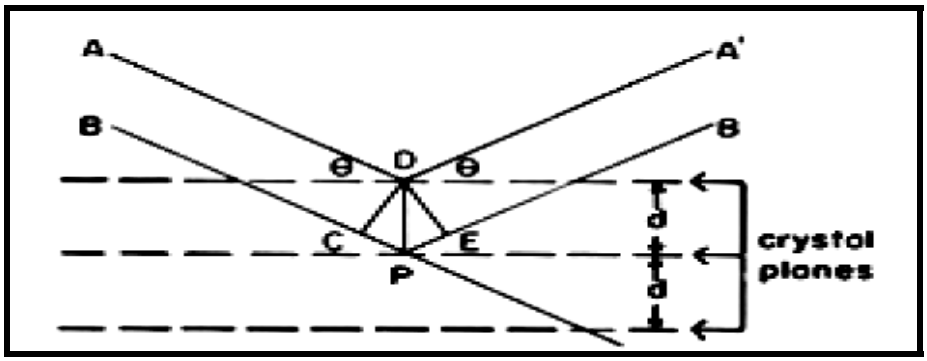


Figure 3.5 Diffraction from crystal planes according to Bragg's Law (Mitchell and Soga, 2005)

In this research, powder XRD was used to determine the crystalline minerals present in the natural soil and also to monitor the mineralogical changes caused by treatment. Samples for XRD test were prepared by grinding the soil using a pestle

and a mortar to a fine homogeneous powder. Then it was placed in the elliptical opening of an aluminum holder and evenly distributed using a microscope slide until a smooth surface was achieved. A Bruker D8 advance diffractometer was used to perform scans in an angle scan (2θ) ranging between 6° to 90° with a 0.02° step size and dwelling time of one second at each step (Figure 3.6). At the end of the test, the mineralogy analysis was carried out based on the characteristic Bragg data available in the standard powder diffraction file (JCPDS, 1995).

Figure 3.6 X-ray Diffractometer

3.4.1.2 Scanning Electron Microscopy & X-ray Spectrometry

It has been well established that the treatment of natural soil with chemical additives will gradually affect the size, shape, and arrangement of soil particles. Furthermore, the degree of improvement is dependent on the quantity and the pattern of new formed products deposited on and around the clay particles.

A JSM-6701F JEOL Field Emission Scanning Electron Microscope (FESEM) was employed to study the morphological changes and the topographic

features associated with clay particles before and after treatment. It incorporates a cold cathode field emission gun, ultra high vacuum, and sophisticated digital technologies for high resolution high quality imaging of microstructures (Figure 3.7). The FESEM images for various mix designs were obtained at 1000×, 5000×, and 10000× magnifications. In addition, it was equipped with Energy Dispersive X-ray spectrometer (EDAX) which enabled a more sophisticated approach regarding the surface composition of particles at different time intervals.

Common minerals found in soils have a definite elemental composition. Therefore for a precise characterization of soil minerals and also to indicate how elements can affect the reaction products, an analysis of major elements present is inevitable. On the other hand, the reaction of chemical stabilizers with clay minerals at room temperatures is usually very slow. This results in a gradual formation of cementitious gel compounds, causing difficulties in their detection using XRD technique. However, this does not mean that these new phases are not formed. In fact, EDAX has proved that they are present (Wild, 1989).

In this method, since each element has a specific and well-defined energy level, the energy differences between shells are used to identify the elements present in the sample. The intensity is determined as a function of the element's concentration and matrix being examined ((counts/sec) vs. (KeV)) (Electroscan, 1996). In this thesis, changes in the Al:Si, Ca:Si, and P:Si ratios of lime and phosphoric acid treated soils were evaluated using the weight percentage results. As a quality assurance measure, multiple samples were analyzed in all cases (at least three) in determining these ratios.

Finally, it should be noted that the sample preparation for FESEM and EDAX analysis involved drying the samples and placing them onto an aluminum stub covered with double-sided carbon tape, and coating the specimen with platinum using a vacuum sputter coater in order to prevent surface charging and loss of resolution.

Figure 3.7 Field Emission Scanning Electron Microscope

3.4.2 Molecular Characterization

3.4.2.1 Nuclear Magnetic Resonance Spectroscopy

In Nuclear Magnetic Resonance (NMR) spectroscopy, the sample is exposed to a magnetic field that allows the atomic nuclei with nonzero spin to absorb electromagnetic radiation, causing the nuclei to switch spin states. The observed NMR frequency of a given nucleus in different parts of a molecule shifts as a result of interaction with fields produced by electrons and other neighboring nuclei. These chemical shifts allow the type of bonds to be identified (Wilson, 1987).

High resolution solid state NMR spectroscopy has become a powerful tool in studying the structure of natural aluminosilicates (Kinsey *et al*., 1985; Engelhardt and Michel, 1987). In particular, ^{29}Si and ^{27}Al Magic-Angle-Spinning (MAS) NMR have provided important information regarding the Si and Al distribution in tetrahedral and octahedral sites, the sequence of charged sheets, and the structural

distortions for a variety of clay minerals such as montmorillonite (Barron *et al*., 1985; Herrero *et al*., 1985; Weiss *et al*., 1987). Nevertheless, much less attention has been devoted to the NMR studies of stabilized soils.

In this thesis, the ^{29}Si and ^{27}Al MAS NMR spectra of untreated and 8 months cured samples were recorded in order to assess the local structure around the Si and Al atoms. The spectra were obtained by a Bruker AVANCE 400 MHz Solid-State NMR instrument using a MAS probe with 7mm Zirconium rotor (Figure 3.8).

3.4.2.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy can be used to identify functional groups by measuring the absorption at characteristic wavelengths of bonds that vibrate independently of one another.

FTIR was performed in an attempt to study the molecular changes in the structure of treated samples. Hence, 2mg of dried soil was ground in an agate mortar and mixed with 200mg potassium bromide (KBr) to form a homogeneous powder, which was then compressed into a solid pellet. The transparent KBr disc (pellet) was then placed in a sample holder where it was scanned using a Perkin Elmer Spectrum 2000 instrument to yield a pattern of the beam transmitted through the sample from 400 to 4000 cm^{-1} (Figure 3.9).

Figure 3.8 Solid-State Nuclear Magnetic Resonance instrument

Figure 3.9 Fourier Transform Infrared device

3.4.3 Leaching Characterization

Leaching test is an essential step in establishing the nature of soil-chemical reactions. In this research, the basis for leaching characterization was to monitor the time-dependent changes in the pore water chemistry in order to determine the chemical composition of the reaction products.

It is worth noting that, although, in an extraction test changing the test parameters such as solid to liquid ratio, test duration, and rotation speed may affect the final equilibrium conditions and hence the resultant chemistry of the leachate. However, since the main focus of this investigation was to assess the relative changes in the solubility of main elements, it was apparent that any of the test parameters could have been chosen so long as the solid to liquid ratio were high enough to avoid over dilution of important elements below the detection limits.

In this research, the leaching was performed following a procedure slightly modified from the Environmental society of Canada (EC, 1990) known as Equilibrium Extraction (EE) test. This method allows the determination of soluble elements using distilled water as the leachant. Hence, 20g of cured sample was placed into a 250mL wide neck plastic bottle. Next, 160mL of distilled water was added and the solution was mixed using a magnetic stirrer for 24h. At the end of mixing, the aqueous phase was separated using filter papers, pH was measured, and the supernatant was preserved for Inductively Coupled Plasma (ICP) analysis of Si, Al, P, and Ca elements (Figure 3.10).

All solutions were filtered through Whatman filter papers. Where gravity filtration was not possible or not completely satisfactory, centrifuging was used. Also, due to the very high cost of ICP analysis, it was important to determine the main elements (i.e., Si and Al) which were more likely to be released into the aqueous solution. Furthermore, clearly, soluble Ca and P had to be measured as well, since their reactions with these elements were of vital interest.

Figure 3.10 Inductively Coupled Plasma spectrometer

3.5 Chemical Properties Analysis

3.5.1 Cation Exchange Capacity

As was comprehensively discussed in the literature review, clay minerals can adsorb cations and anions and retain them in an exchangeable form. The CEC_p is defined as the cation exchange capacity (CEC) attributed to the permanent charges of the clay structure. The methods of measurement are usually based on determining the quantity of a particular exchangeable cation by chemical and spectroscopic means and expressing the result per 100g of the dry soil.

Although, no general method exist that can be reliably used to determine the CEC value. However, the use of divalent Barium (Ba^{2+}) as a saturating cation is considered to be more effective, especially in determining the CEC for kaolinite minerals (Tan, 2005). In this thesis, the revised version suggested by Tan and Dowling (1984) was used for CEC_p measurements. In order to determine the CEC_p

caused by permanent charges, it was necessary to block the variable exchange sites. This was achieved by acidifying the soil so that the cations on the variable sites were replaced by protons. Hence, 10g of the soil were placed into a 100mL polyethylene centrifuge tube. Next, 30mL of 0.1M HCL was added, and the bottle was shaken for 15min with a mechanical shaker. Then, the sample was centrifuged at 6,000rpm for 20min, and the supernatant was discarded very carefully to avoid loss of solids. To the acidified soil 50mL of 0.3M $BaCl_2$ solution was added. The mixture was shaken for 30min with a mechanical shaker and the supernatant was discarded from the centrifuged sample. After the clay material had been saturated with Ba^{2+} ions, the sample was washed two times with 50mL of distilled water to remove non-exchanged Ba^{2+} ions. In the next step called the extraction step, after the addition of 50mL of 0.3M $CaCl_2$ solution to the washed Ba-saturated soil, the sample was shaken for 30min, centrifuged, and the supernatant was collected carefully into a 100mL volumetric flask. The washing step was performed one more time with 30mL of distilled water. The centrifuged wash water was added to the solution in the volumetric flask. Finally, the extracted solution was analyzed for Ba concentration using an ICP spectrometer, and the CEC_p value (mEq/100g) for each sample was determined from the results (refer to **Appendix D** for calibration of ICP for Ba analysis).

3.5.2 Thermal Gravimetric Analysis

It has been suggested that organic matter can retard or prevent the proper action of chemical stabilizers on the clay structure. One reason for such behavior is the great affinity of organic particles in adsorbing ions present in the pore water. Also because of their complex nature, various types of reactions are feasible in the soil medium.

Thermal Gravimetric Analysis (TGA) was employed to determine the amount of organics present and also to study the thermal properties of the treated samples. This method is based on monitoring the weight loss of the material during a

controlled heating process in a defined gas atmosphere. This is an important advantage, since some clay minerals such as montmorillonite and kaolinite can lose up to 20% and 3% of their mass at low temperatures, respectively. The latter is caused by dehydration and should not be mistakenly considered as part of the organic fraction (Al-Khafaji and Andersland, 1992).

A TGA/SDTA851 instrument which is a modern device for TGA and simultaneous difference thermal analysis (SDTA) of materials was used in this investigation (Figure 3.11). Hence, small amounts of the sample was placed in an aluminum crucible under N_2 gas atmosphere with a flow rate of 10 mL/min and analyzed up to 850 ºC at a rate of 10 ºC/min.

Figure 3.11 Thermal Gravimetric Analyzer

3.5.3 pH Measurement

The pH of soil solution provides useful information regarding soil-chemical reactions as it reflects the changes occurring in the medium. Also, as was seen before soil pH influences the distribution of charge on clay lattice and is a controlling factor in the solubility of clay minerals. These effects are of greatest importance in the stabilization process and should be considered carefully.

In this study, a Hannah model HI 8424 pH meter (Figure 3.12) was used to measure the pH value of treated samples according to BS 1377: Part 3: 1990 (clause 9.1). The data were obtained in triplicate, and the average pH was reported. In addition, three commercially available pH buffers (pH 4, pH 7, and pH 9.2) were used to calibrate the instrument prior to each measurement (refer to **Appendix C** for calibration of pH meter). Also for convenience, in conjunction with the pH electrodes, an automatic temperature compensation probe was employed to correct pH readings to the equivalent pH at 25^{o}C. After conducting the test, all electrodes were cleaned according to the manufacturer's instructions. However, after use in Bentonite samples, it was necessary to stand the electrode in a strong detergent to remove residue and to keep the electrode within the required operating parameters.

Figure 3.12 pH measurement equipment

3.6 Physical Properties Analysis

3.6.1 Unconfined Compressive Strength

In soil stabilization studies, Unconfined Compressive Strength (UCS) is the strength characteristic commonly used to evaluate the degree of improvement in the engineering properties of treated samples due to the formation and hardening of cementitious materials.

In this research, UCS test was carried out in accordance with BS 1924: Part 2: 1990 (clause 4.1), with at least three specimens being tested for each mix design. Hence, after reaching the specified curing time, samples were taken from the thin wall PVC tubes and directly tested at an axial strain rate of one percent per minute. During the test, the applied load and changes in the axial deformation were recorded automatically by the data acquisition unit (ADU) with failure being defined as the peak axial stress. At the end of each test, the failed soil specimen was dried and weighed to determine its moisture content. In Figure 3.13, the setting up for the UCS test in a triaxial loading frame is presented. It should be noted that, prior to conducting the tests at the three stages of curing, the two transducers (LVDT) for measuring vertical displacement and axial load were calibrated.

Figure 3.13 Triaxial loading frame, ADU, and the processing unit

3.6.2 Surface Area Value

One of the most common methods for determining the surface area of finely divided materials is that of Brunauer, Emmett and Teller (1938), known as the BET method. The method is based on collecting isotherm data for the physical adsorption of an inert gas and modeling the adsorption data using the following BET isotherm equation (Rauch, 2003):

$$(\nu/\nu_m) = c(P/P_0)/\{(1-(P/P_0)[1+(c-1)(P/P_0)]\} \quad (3.3)$$

where:

ν = volume of gas adsorbed per unit weight of clay at a pressure P

ν_m = volume of gas adsorbed for monolayer coverage

(P/P_0) = partial pressure of the gaseous adsorbate

c = constant

In this research, the technique was used to observe changes in the surface area of lime and phosphoric acid stabilized soil samples with curing time. The surface area value was obtained by physical adsorption of nitrogen gas using Quantachrome Autosorb-1 surface area analyzer (Figure 3.14). This instrument is designed for the surface area analysis of powdered and porous materials. In addition, it is microprocessor controlled and communicates with a XP-based PC with the dedicated data processing software which makes it ideal for physisorption analysis. Hence, approximately 0.15g of the cured sample was deposited in the sample holder. After degassing for 20hr at 300°C, nitrogen gas was injected and the surface area value was calculated using the multipoint BET method (Quantachrome, 2007).

It should be noted that since nitrogen does not penetrate into the inner layer of clay particles during a BET analysis, the pores in this case correspond to the pore space between individual clay particles.

Figure 3.14 Surface Area measurement device

3.7 Summary

The literature review reported the current scientific understanding of soil stabilization. These findings formed the basis for selecting the most appropriate methods of analyzing soil-chemical interaction.

The primary objective of this thesis was to identify the various processes controlling the stabilization mechanisms and also to obtain direct structural information on the reaction products. Hence, in order to fulfill our goals, it was necessary to understand the relationship between the chemistry of pore water, the chemical composition on the surface of soil particles, and the changes induced in the soil-stabilizer matrix. Hence, data for characterization study of phosphoric acid and lime treated soil samples, at different time intervals, were obtained from X-ray Diffractometry (mineralogy), Fourier Transform Infrared Spectroscopy (functional groups and type of bonding), Nuclear Magnetic Resonance spectroscopy (molecular structure), Energy Dispersive X-ray Spectrometry (surface chemical composition), Field Emission Scanning Electron Microscopy (morphology), Cation Exchange

Capacity (structure chemistry), BET surface area (particle size), and leaching test (pore water chemistry) analysis.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In previous chapter, the methods implemented for laboratory investigations of the treated samples were presented in an order which allowed the effects of stabilizers on soil's mineralogy, fabric, local bonding, and pore water chemistry to be monitored initially. As clearly evident, the results obtained from these tests are inter-related. Hence, in this chapter they are presented in a sequence that the most important aspect of soil-stabilizer interaction is highlighted initially and which it can be used to interpret and explain the data obtained from the other tests. The results reported in this chapter are divided into the following categories:

a) Basic properties of the materials used in the laboratory investigation.

b) The time-dependent changes in the soluble chemistry of pore water based on soil and stabilizer type.

c) The micro-structural developments of treated samples.

d) The effect of stabilizers on the molecular structure and local bonding.

e) Variations in the physical properties of stabilized soil in terms of unconfined compressive strength and surface area.

4.2 Material Properties

4.2.1 Particle Size Distribution

In soft soil deposits, clay fraction of the soil plays an important role in determining the effectiveness of the stabilization technique. This is mainly due to the active nature of clay minerals and their ability to interact with other ions present in the environment. According to British Standard terminology, the clay fraction of a soil is composed of particles finer than 2μm that can be made to exhibit plasticity within a range of water contents. Furthermore, the particle size distribution is defined as the percentages of various grain sizes present in a material as determined by sieving and sedimentation.

Results of the particle size analysis and hydrometer test are shown in Table 4.1 and Figure 4.1, respectively. As can be seen, the natural Green Bentonite and Laterite Clay had the highest amounts of clay constituents in the mix designs. This was important since it is directly linked to the surface area available for the soil-chemical reactions.

Table 4.1 : Percentages of various particle sizes present in the natural soil

Soil Type	Size Description			
	Gravel (60.0-2.0mm)	Sand (2.0-0.06mm)	Silt (0.06-0.002mm)	Clay (<0.002mm)
Green Bentonite	0.0	0.0	21.8	78.2
Laterite Clay	0.0	15.4	23.7	60.9
White Kaolin	0.0	6.7	51.2	42.1
Pink Soil	0.0	52.6	38.2	9.2

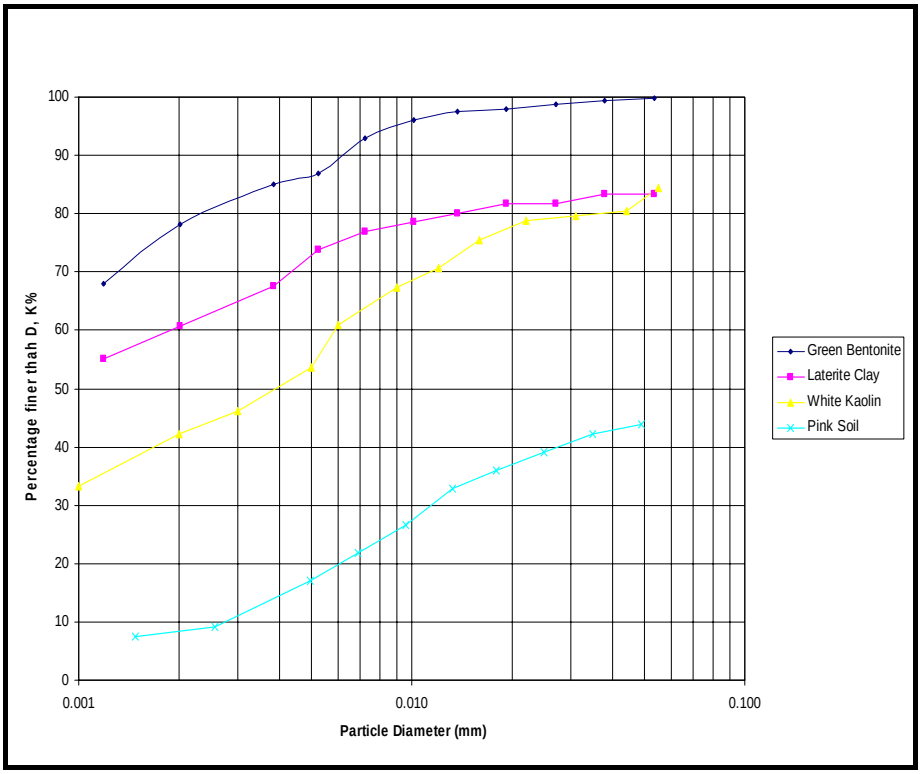


Figure 4.1 Particle size distribution curve of the natural soil

4.2.2 Compaction Characteristics

As was explained in the previous chapter, in this study all mix designs of a particular soil were compacted at the optimum moisture content of the natural soil. Therefore, a separate dry density-water content curve for lime and phosphoric acid treated samples was not determined. The Optimum Moisture Content (OMC) and Maximum Dry Density (MDD) of each individual soil is summarized in Table 4.2.

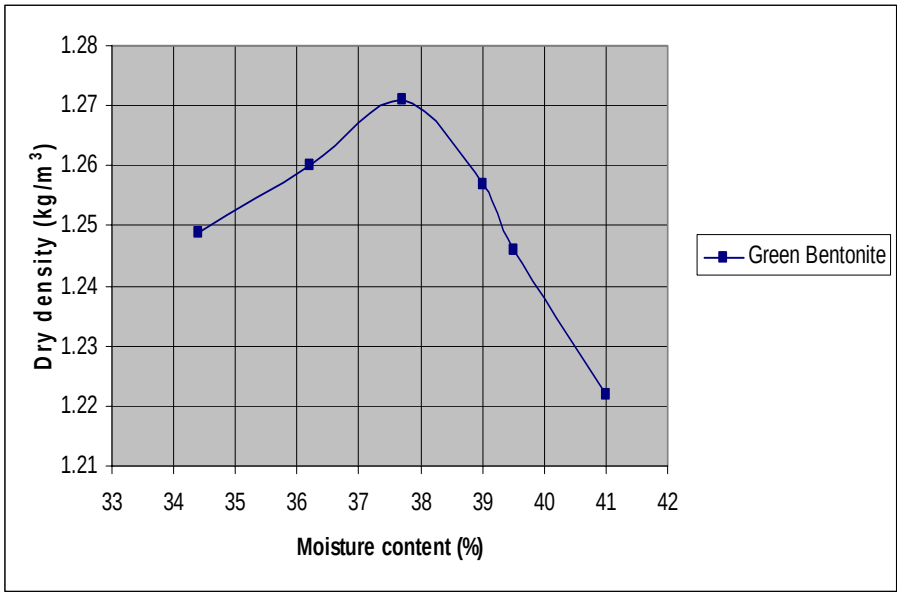
In Figures 4.2 and 4.3, the dry density-water content relationships for the four soils are illustrated. It should be noted that each point on the graph was the average dry density of four samples compacted at the same water content.

Table 4.2 : Compaction specifications of the natural soil

Description	Soil Type			
	Green Bentonite	**Laterite Clay**	**White Kaolin**	**Pink Soil**
Optimum moisture content (%)	37.70	34.00	18.40	20.00
Maximum dry density (Mg/m^3)	1.271	1.334	1.641	1.582
Compaction hammer mass (kg)	2.5	2.5	2.5	2.5
Compaction hammer fall height (mm)	300	300	300	300
Number of compaction layers in mould	3	3	3	3
Number of drops per layer	27	27	27	27
Applied compactive effort (kJ/m^3)	596	596	596	596

4.2.3 Initial Consumption of Lime Test

Figures 4.4 and 4.5 demonstrate the results of adapted and standard Initial Consumption of Lime (ICL) test. From the adapted ICL test performed on Green Bentonite soil it was evident that the need to dilute the solution in order to perform the test affected the ICL value. This was expected since the addition of excess water would reduce the pH of the solution, particularly at lower lime contents. Nevertheless, at higher lime concentrations the ICL changes were relatively small and a value of 7% for Bentonite sample was likely to be reasonably accurate. The results also indicated that the percentage of lime required for satisfying all the short-term reactions was strongly dependent on the clay content and more importantly the type of minerals present in the soil medium. For instance, in a clay with predominantly pH-dependent surface adsorption sites such as White Kaolin, very little lime was needed to achieve the ICL value of 1.5%. This was due to the fact that after lime addition, the increase in number of negative charge sites created on the surface of clay particles, attracted Ca^{2+} ions and moved the dissolution equilibrium of $Ca(OH)_2$ to release more Ca^{2+} ions and OH^- ions into the solution which eventually resulted in noticeable pH gains. Furthermore, in contrast to soils with high cation exchange capacity such as Green Bentonite, fewer Ca^{2+} or OH^- ions were involved in immediate chemical interactions with the soil minerals.



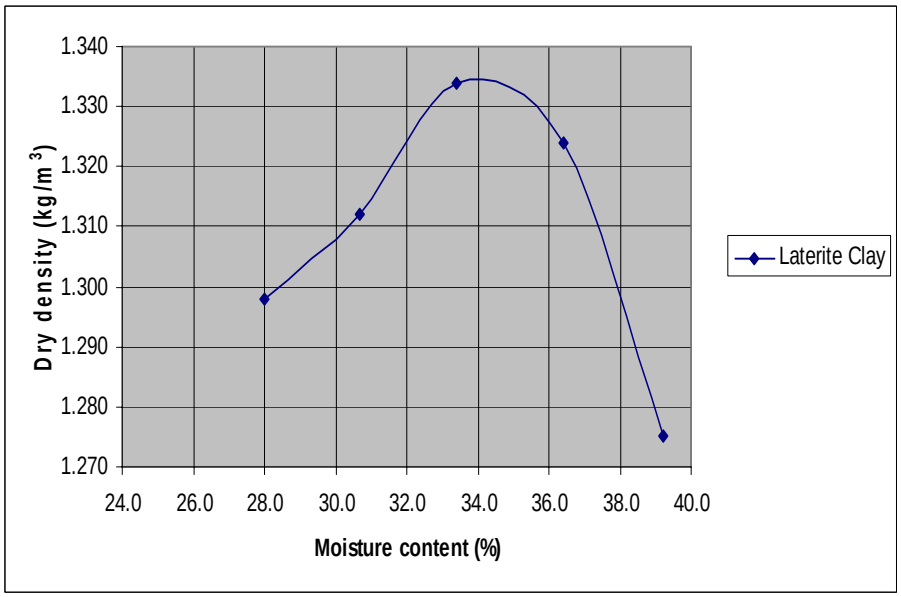
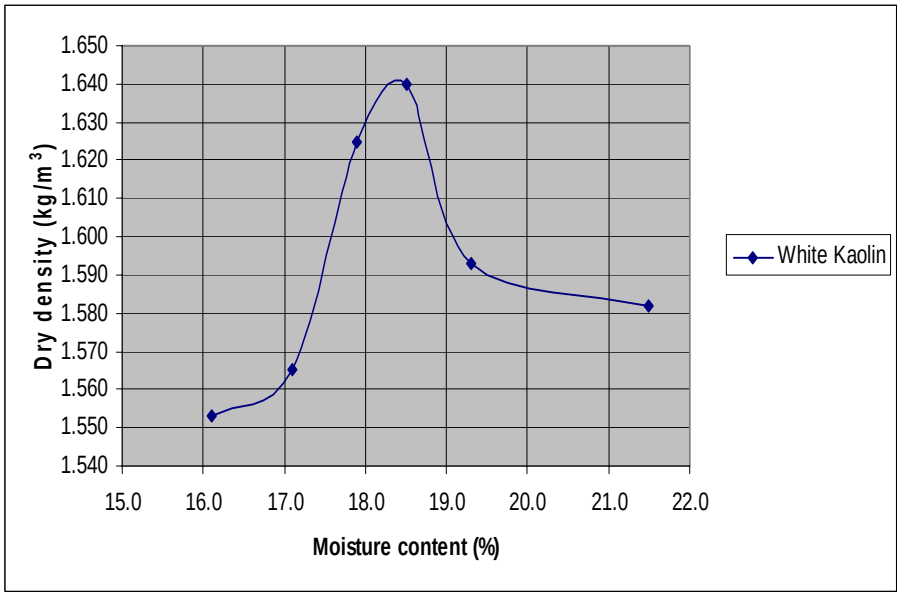


Figure 4.2 Variation of dry density with water content for Green Bentonite and Laterite Clay samples



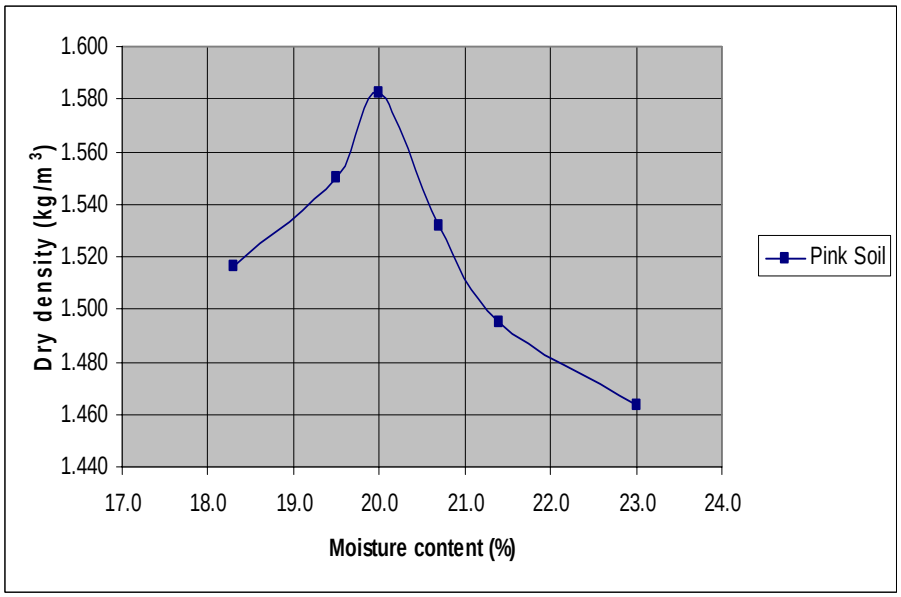
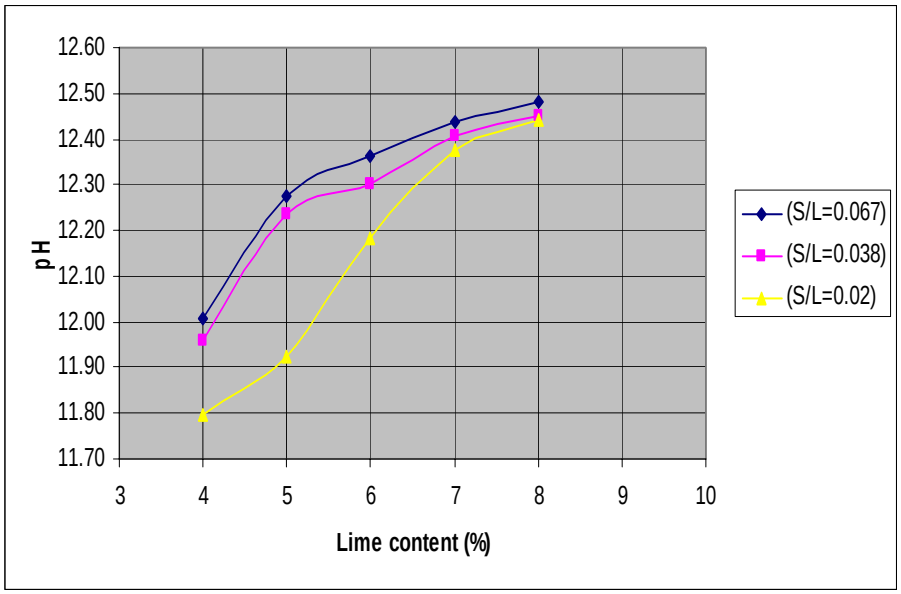


Figure 4.3 Variation of dry density with water content for White Kaolin and Pink Soil samples



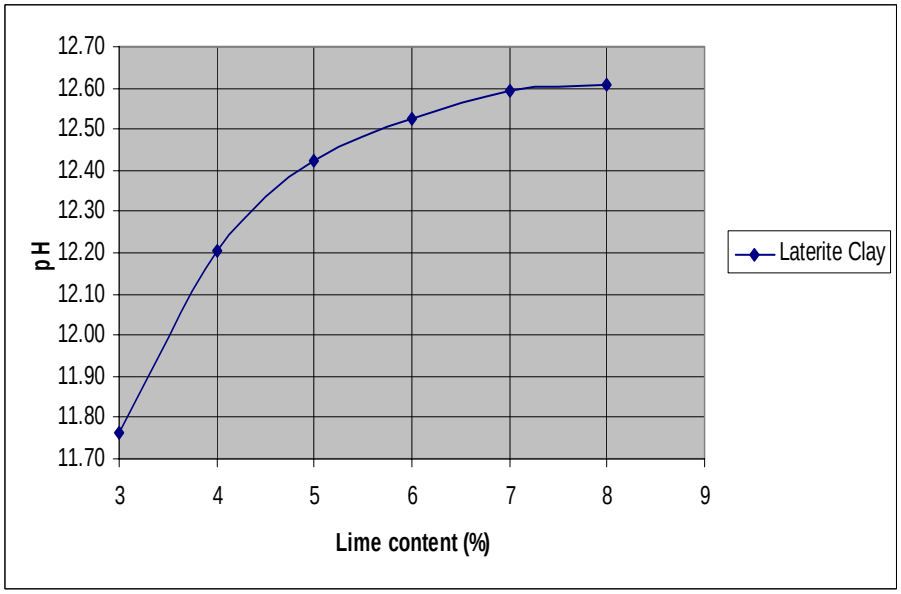
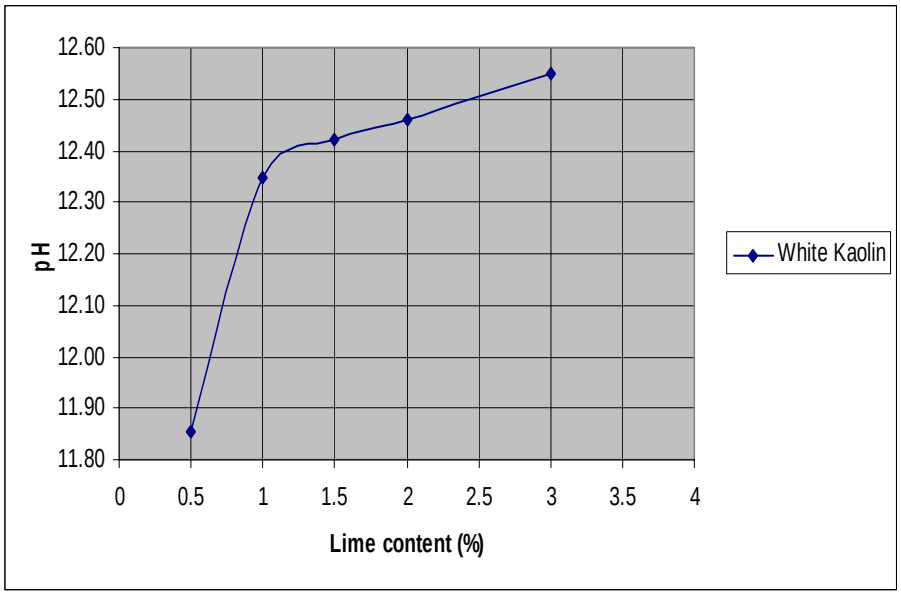


Figure 4.4 Results of the ICL test on Green Bentonite and Laterite Clay



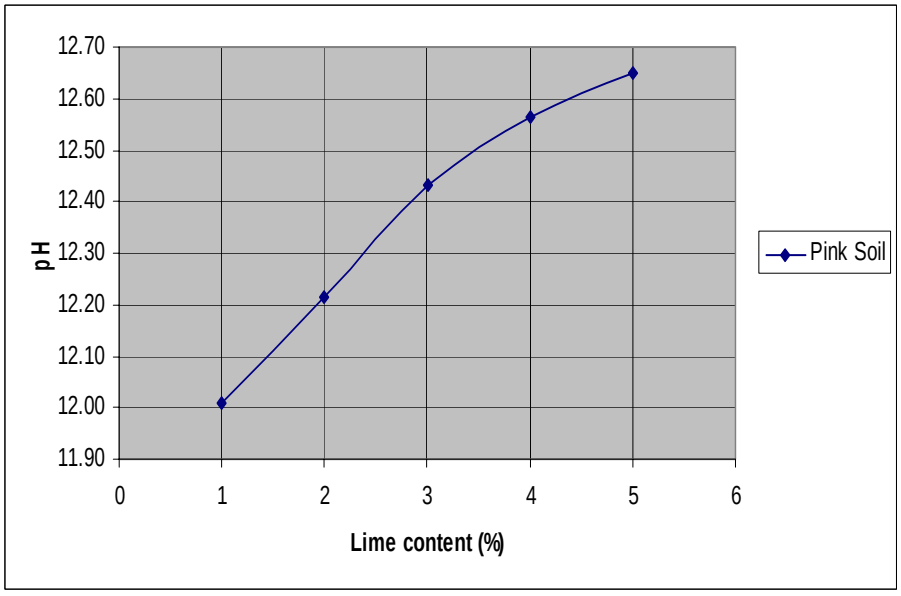


Figure 4.5 Results of the ICL test on White Kaolin and Pink Soil

4.3 Characterization of Cured Samples

4.3.1 Leaching Results

In recent years, much of the investigations conducted on the leaching characteristics of soils have been focused on monitoring the mobility of metals from the contaminated sites into the surrounding environment.

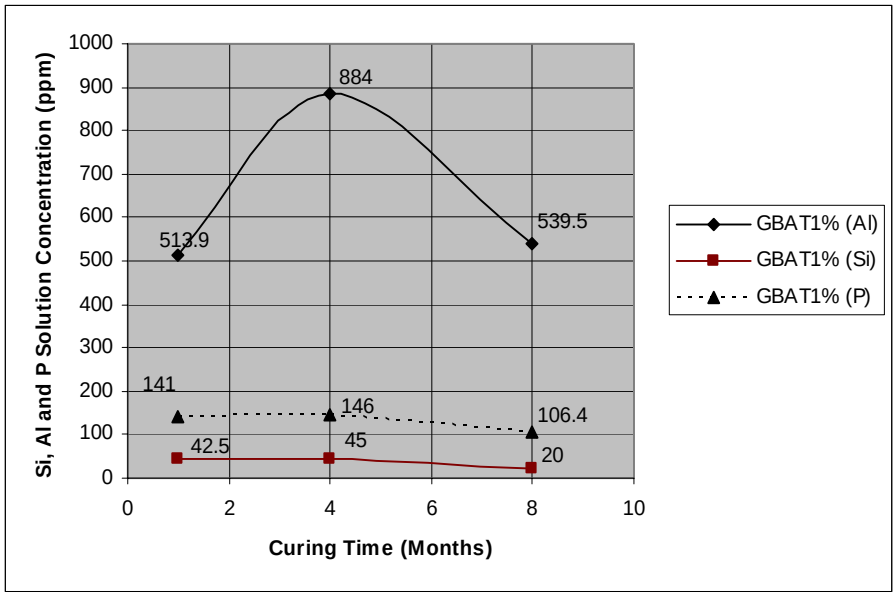
Leaching analysis can provide valuable information regarding the time dependent changes in the structure of soil-stabilizer matrix. The soluble concentration of P, Al and Si in 1% and 7% phosphoric acid treated Bentonite samples are presented in Figure 4.6 (refer to **Appendix A** for data obtained from leaching test). As can be seen, after 4 months of curing, the level of soluble P and Al in the aqueous solution appeared to have reached an optimum. With further curing to 8 months, a reduction in the concentration of soluble Al and P were observed. This can be explained via the re-crystallization process of reaction products which were mainly comprised of these elements. Furthermore, in contrast to lime treatment, the soluble Al release was more prominent than the soluble Si release.

Figure 4.7 shows the time-dependent changes in the soluble concentration of Si, Al and Ca elements on addition of 3% and 10% lime and after centrifugation and gravity filtration of the solutions, respectively. As can be seen, the level of soluble Si was much higher than the soluble Al concentrations which remained quite low at all curing periods. This was due to the fact that the majority of edge sites in montmorillonite minerals were associated with the tetrahedral silicate structure. It was also rational that if OH^- ions were attracted to Ca^{2+} ions on the exchange sites, then mineral dissolution could also be initiated at these sites, adjacent to tetrahedral silicates. After 1 month, the amount of Si released to the aqueous solution from both lime mix designs had the highest value while reaching a constant after 4 months curing. This suggested that in Bentonite soils most of the clay-lime reactions occurred at the first 4 months period. On the other hand, similar to phosphoric acid treatment, with increasing curing time to 8 months, the soluble Ca plot revealed a

downward trend in the level of Ca released to the solution. This was consistent with the incorporation of Ca into reaction products. A similar trend in Si, Al and Ca variations on lime treatment has been reported by Boardman *et al.* (2001).

It should be noted that, due to the problems associated with the gravity filtration of Green Bentonite samples containing 1% phosphoric acid and 3% lime, aggressive centrifugation process was used to separate the solids from the solution, therefore, the results obtained from these samples must be interpreted very cautiously. Nevertheless, the same behavioral trend in comparison to other phosphoric acid and lime design mixes were observed, although it was clearly of a greater magnitude. The latter was probably caused by the aggressive action of centrifugation.

The concentrations of soluble Si, Al, and P or Ca elements released from Laterite Clay samples into the aqueous solution are shown in Figures 4.8 and 4.9, respectively. As can be seen, the 7% phosphoric acid stabilized soil released approximately 66ppm soluble P at the early stages of curing while reaching an optimum of approximately 171ppm after 4 months curing. The former was probably due to the reaction of free iron and aluminum oxides present in the soil environment with phosphoric acid which resulted in a relatively lower P concentration at 1 month curing period. On the other hand, considering the weathering action of the acid on the soil structure and bearing in mind the high phosphate content of the tropical soil, an increase in the level of soluble P with curing time was justifiable. With further curing to 8 months, a downward trend in the soluble P concentration was observed. On the other hand, in the 3% and 7% lime stabilized soil, the soluble Ca concentration decreased sharply with curing time. The reduction in the level of stabilizer ions extracted from soil matrix was consistent with the formation of new reaction products which rendered them less soluble.



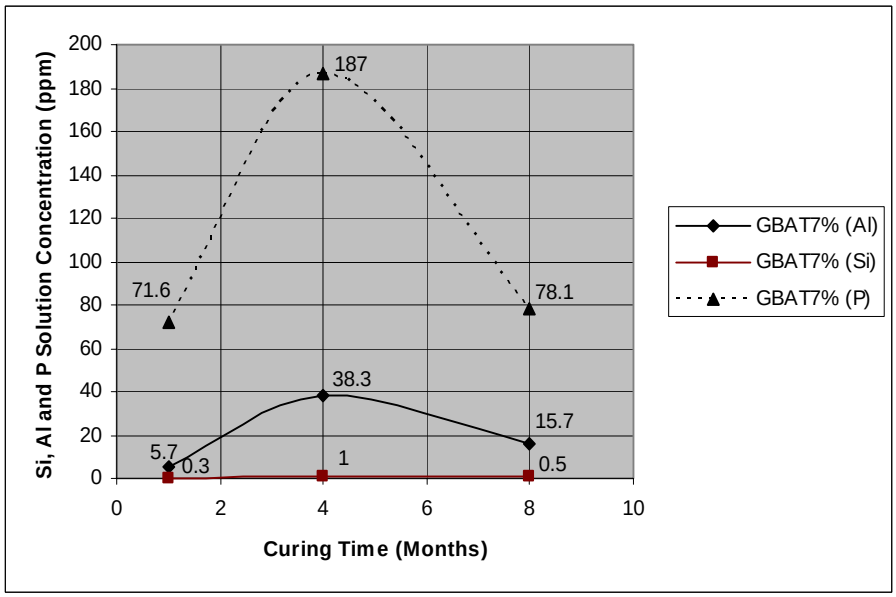


Figure 4.6 Levels of soluble Al, Si, and P release into the aqueous solution with respect to 1% and 7% phosphoric acid treatment for Green Bentonite samples

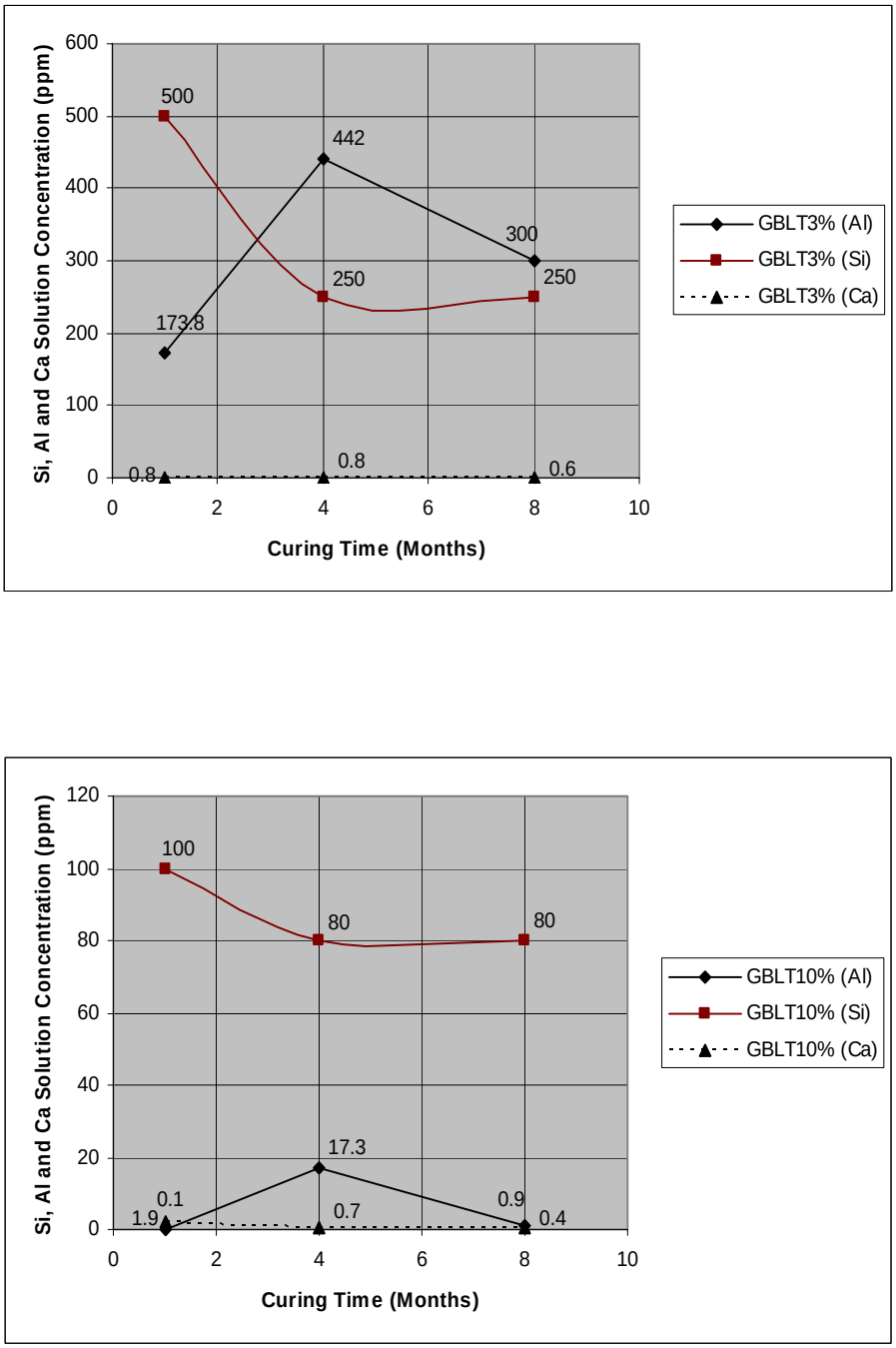


Figure 4.7 Levels of soluble Al, Si, and Ca release into the aqueous solution with respect to 3% and 10% lime treatment for Green Bentonite samples

Consideration of the soluble Al data in both graphs revealed some interesting points. As apparent, the Al release for 7% acid treated samples seemed to increase with curing period while in contrast, the Al concentration of solutions stabilized with lime showed a significant decrease, with a sharp reduction occurring in the first 4 months. The former can be attributed to the highly acidic nature of pore water which resulted in the dissolution of clay alumina and the free aluminum oxides present in the soil environment. While the latter was likely to be caused by the coating action of free oxides and their lower dissolution in an alkaline environment in comparison to the acidic medium which prevented the attack of lime on the clay mineral structure. This also might have been the main reason responsible for the little release of Si in lime design mixes. However, it was found that that when 1% phosphoric acid was added to the Laterite Clay samples, Si became the most susceptible to dissolution. An initial suggestion could be the fact that at some hydroxyl site due to the acidic conditions, positive charges were developed which initiated the repulsion of excess H^+ ions from these sites and their attraction to the electronegative oxygen associated with the silicon atoms where dissolution occurred. Also as was clearly apparent, similar to Bentonite samples, with respect to phosphoric acid and lime design mixes, the same trend for P and Ca plots were observed.

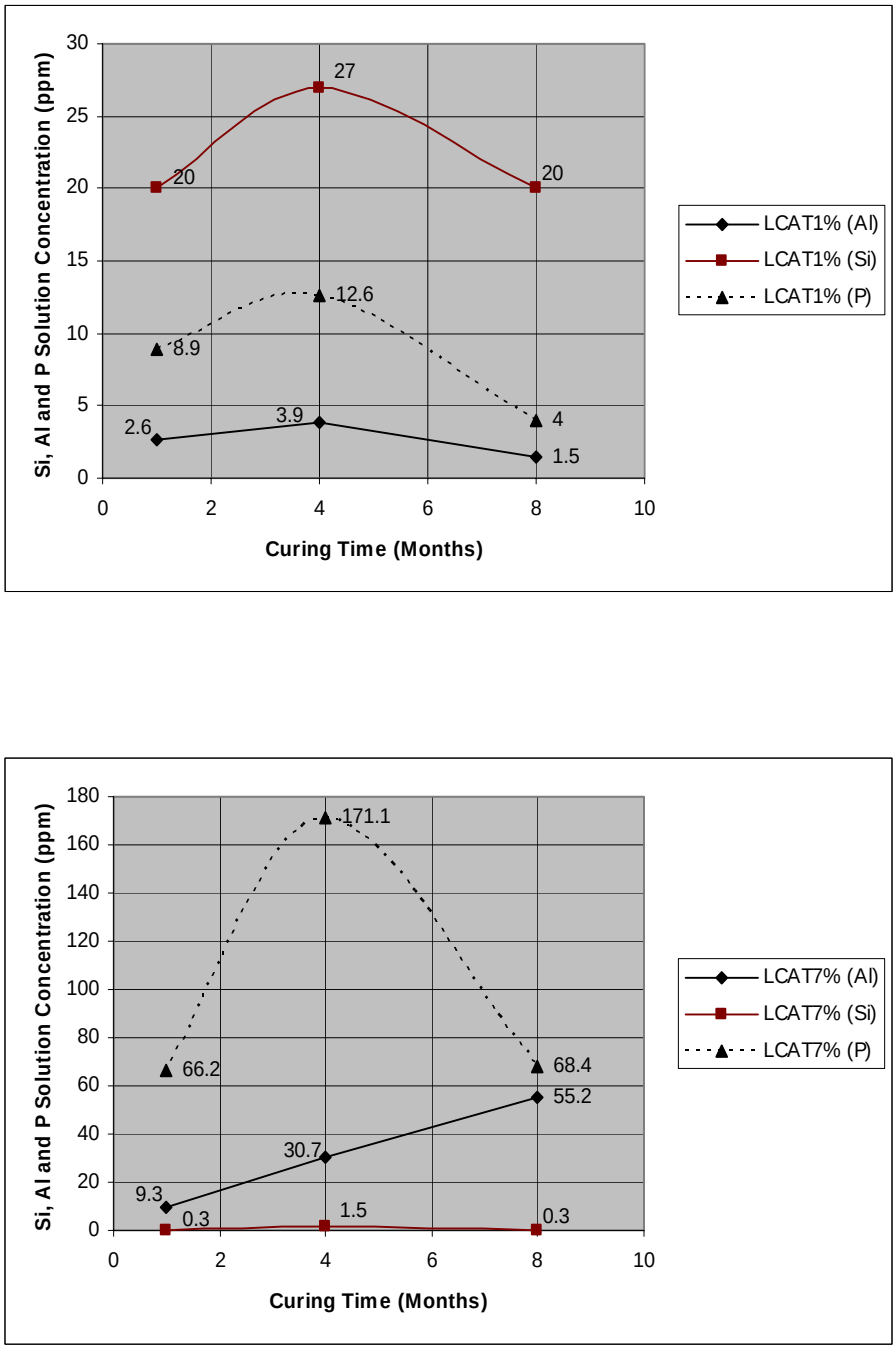
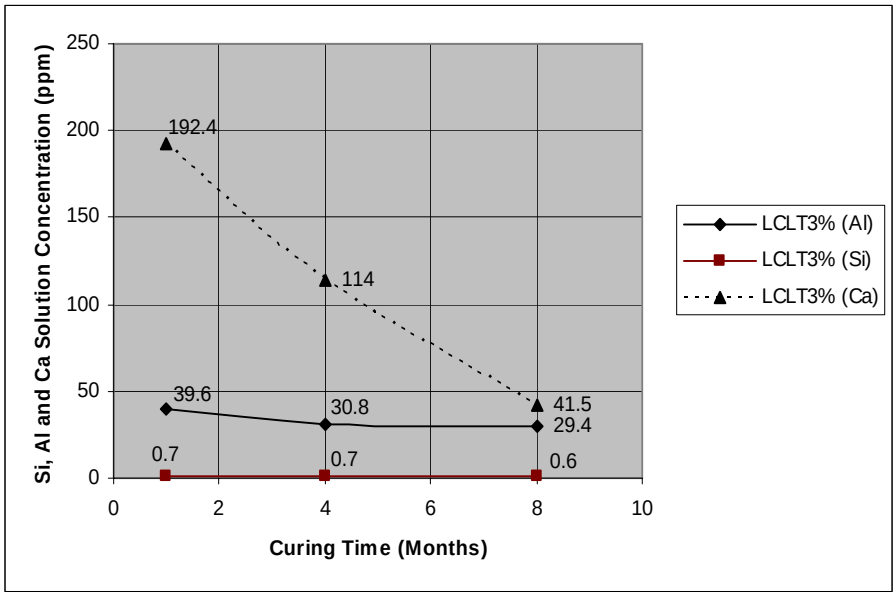


Figure 4.8 Levels of soluble Al, Si, and P release into the aqueous solution with respect to 1% and 7% phosphoric acid treatment for Laterite Clay samples



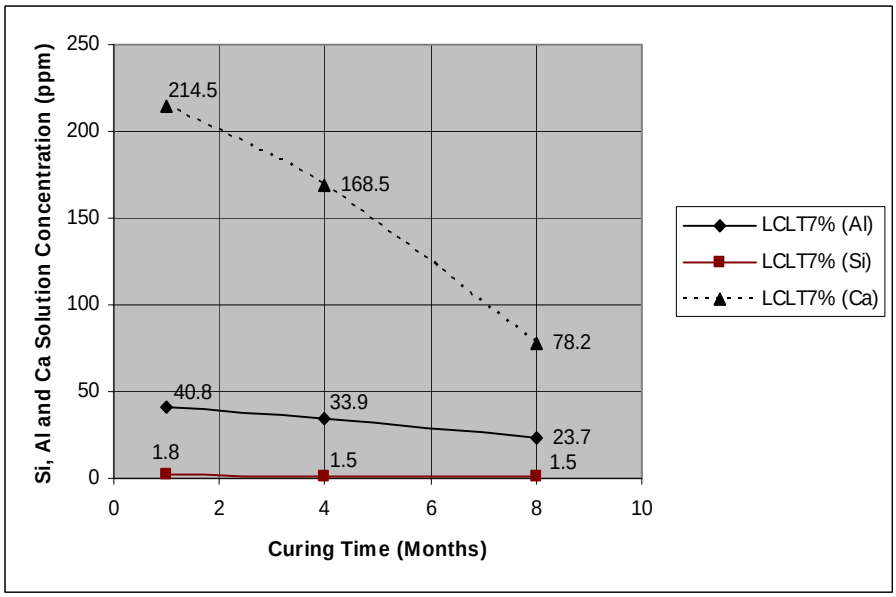
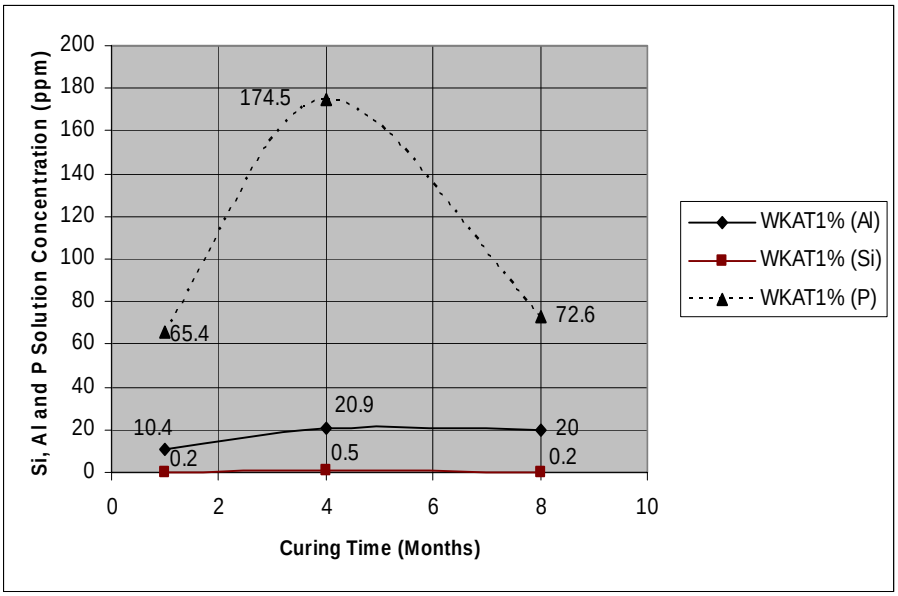


Figure 4.9 Levels of soluble Al, Si, and Ca release into the aqueous solution with respect to 3% and 7% lime treatment for Laterite Clay samples

The release of soluble Al, Si, P or Ca from phosphoric acid and lime treated White Kaolin samples at different time intervals are shown in Figures 4.10 and 4.11, respectively. As seen in the lime stabilized soil, with increasing curing time there was a sharp reduction in the level of Ca monitored in the aqueous solution. This was consistent with the incorporation of Ca ion into the reaction products. On the other hand, the 5% phosphoric acid treated samples released a soluble P concentration of 67.5ppm at 1 month curing period while reaching an optimum of approximately 184ppm after 4 months. This behavior confirmed the formation of inner-sphere complexes between the phosphate ion and the surface hydroxyl groups at the early stages of curing. Also due to the amphoteric nature of alumina, positive charged sites were developed at the edges of kaolinite minerals, thus attracting P ions to these sites. With further curing to 4 months, an increase in the level of soluble P was observed. This was caused by the weathering action of acid on the soil structure. It should be noted that the reduction in the level of soluble P at longer curing periods was consistent with the formation of new reaction products which rendered them less soluble.

According to the soluble Al data from both plots, the acid treatment caused much higher release of Al than the lime treated samples, while virtually reaching a constant value after 4 months curing period. This could be explained through the time-dependent weathering action of phosphoric acid and the higher solubility of Al ions in a low pH environment (Brady and Weil, 1999). On the other hand, for all mix designs, little soluble Si concentrations were observed. The reason responsible for this type of behavior was the fact that, the hydroxyl groups exposed at the surface of kaolinite particles were strongly pH sensitive. Therefore at high pH, there was a greater tendency for H^+ from the hydroxyls to go into the solution. This tendency in turn initiated mineral dissolution directly next to a source of alumina in the clay structure. On the other hand, at low pH since the hydroxyl sites became positively charged the clay alumina was released from surface sites by protonation action. It worth noting that a similar trend in Si, Al and Ca release of lime stabilized kaolin soils has been reported by Boardman *et al*. (2001).



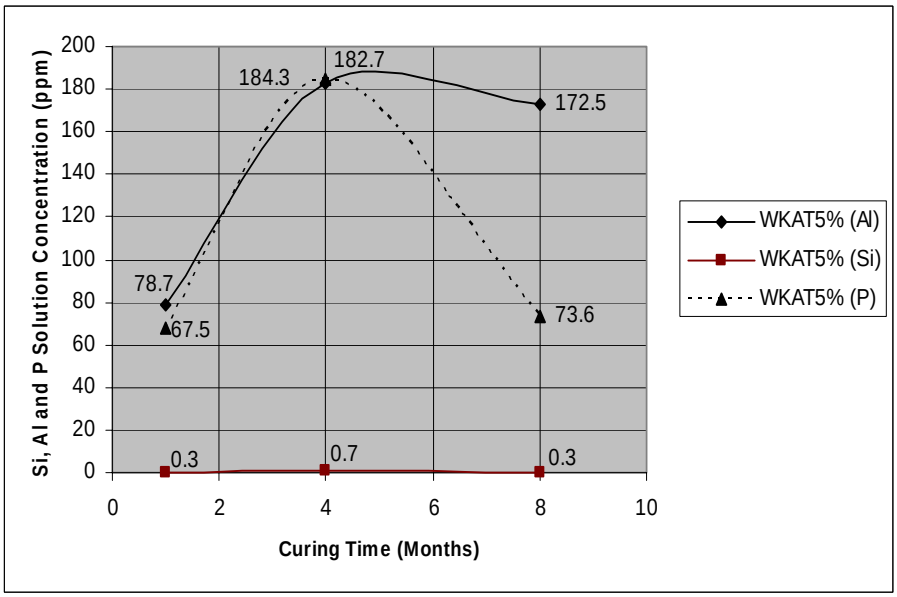
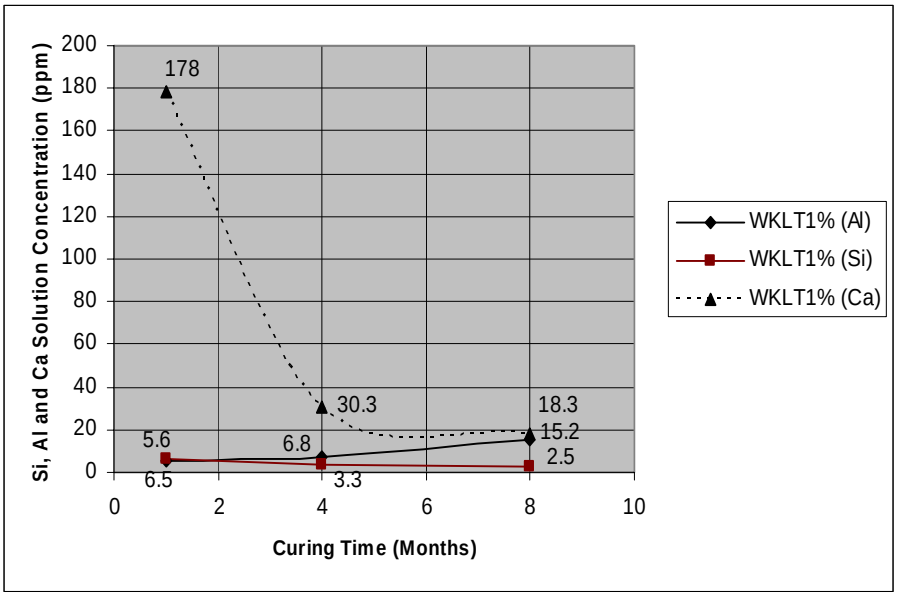


Figure 4.10 Levels of soluble Al, Si, and P release into the aqueous solution with respect to 1% and 5% phosphoric acid treatment for White Kaolin samples



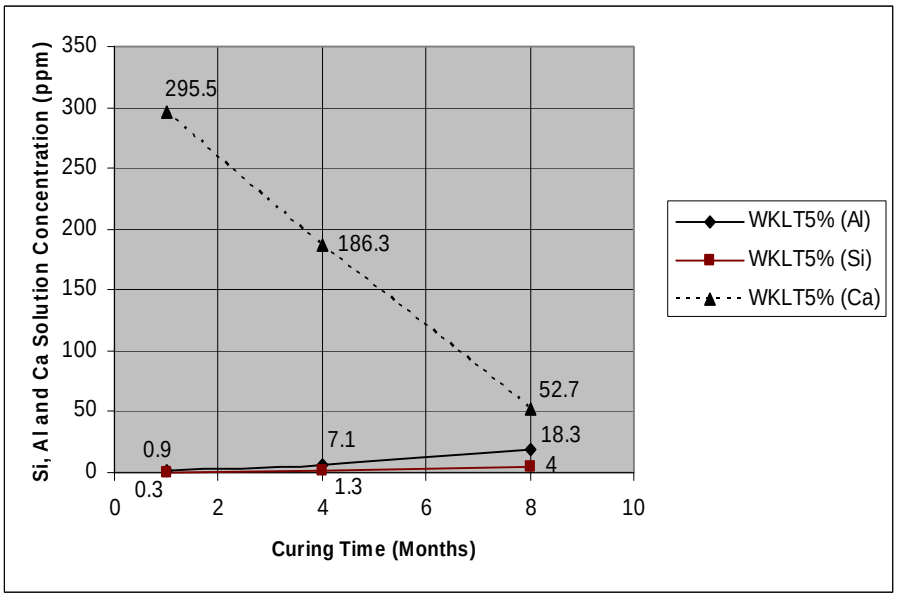


Figure 4.11 Levels of soluble Al, Si, and Ca release into the aqueous solution with respect to 1% and 5% lime treatment for White Kaolin samples

The concentrations of soluble Al, Si, and P or Ca elements released from Pink Soil samples are shown in Figures 4.12 and 4.13. As can be seen, the 5% phosphoric acid stabilized soil released approximately 67ppm soluble P at the early stages of curing while reaching an optimum of approximately 183ppm after 4 months curing. The former was probably due to the diffusion of phosphate ion into the soil structure which resulted in a relatively lower P concentration at 1 month curing period. On the other hand, considering the weathering action of the acid on the soil structure, an increase in the level of soluble P with curing time was justifiable. With further curing to 8 months, a downward trend in the soluble P concentration was observed. On the other hand, in the 1% and 5% lime stabilized soil, the soluble Ca concentration decreased sharply with curing time.

The data obtained from ICP analysis also illustrated that on addition of lime and phosphoric acid to Pink Soil samples, only Al appeared to become soluble with curing time with no measurable Si activity. In addition, consideration of the soluble Al data in both graphs revealed some interesting points. As apparent, the Al release for 5% acid and lime treated samples seemed to be the highest at 1 month curing period. With increasing curing time, the Al concentration of solutions showed a significant decrease, with a sharp reduction occurring after 4 months. This suggested that in Pink Soil design mixes most of the clay-chemical reactions occurred at the first 4 months period.

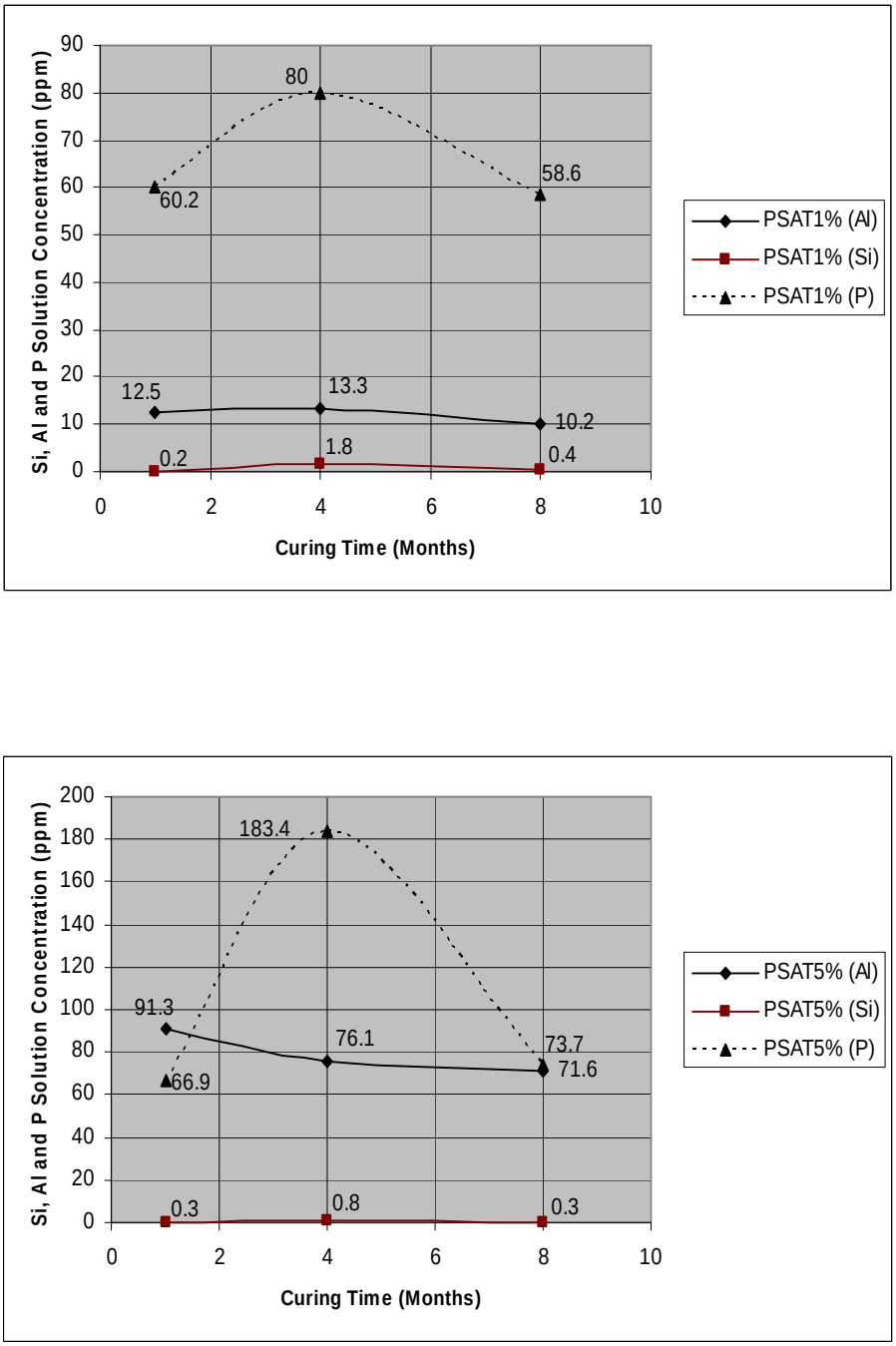
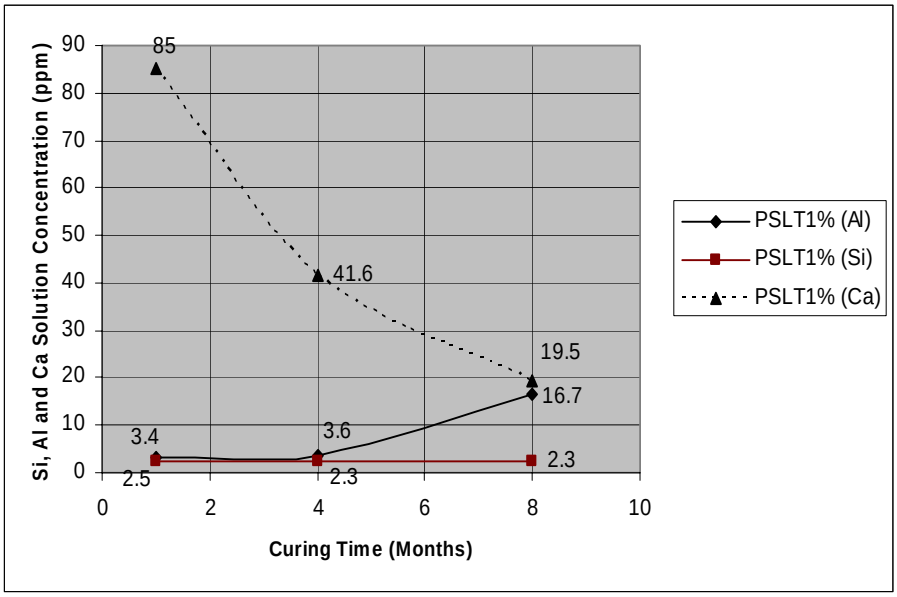


Figure 4.12 Levels of soluble Al, Si, and P release into the aqueous solution with respect to 1% and 5% phosphoric acid treatment for Pink Soil samples



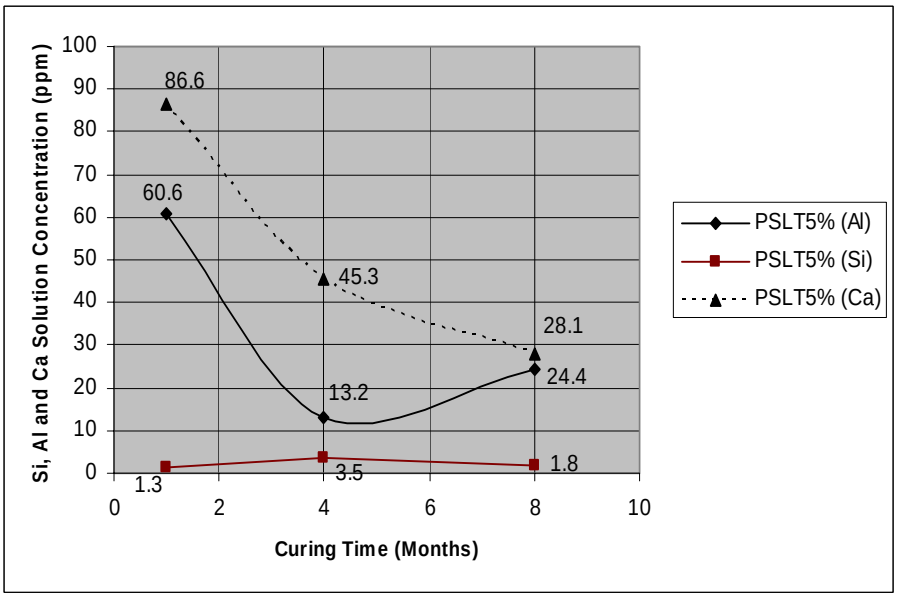


Figure 4.13 Levels of soluble Al, Si, and Ca release into the aqueous solution with respect to 1% and 5% lime treatment for Pink Soil samples

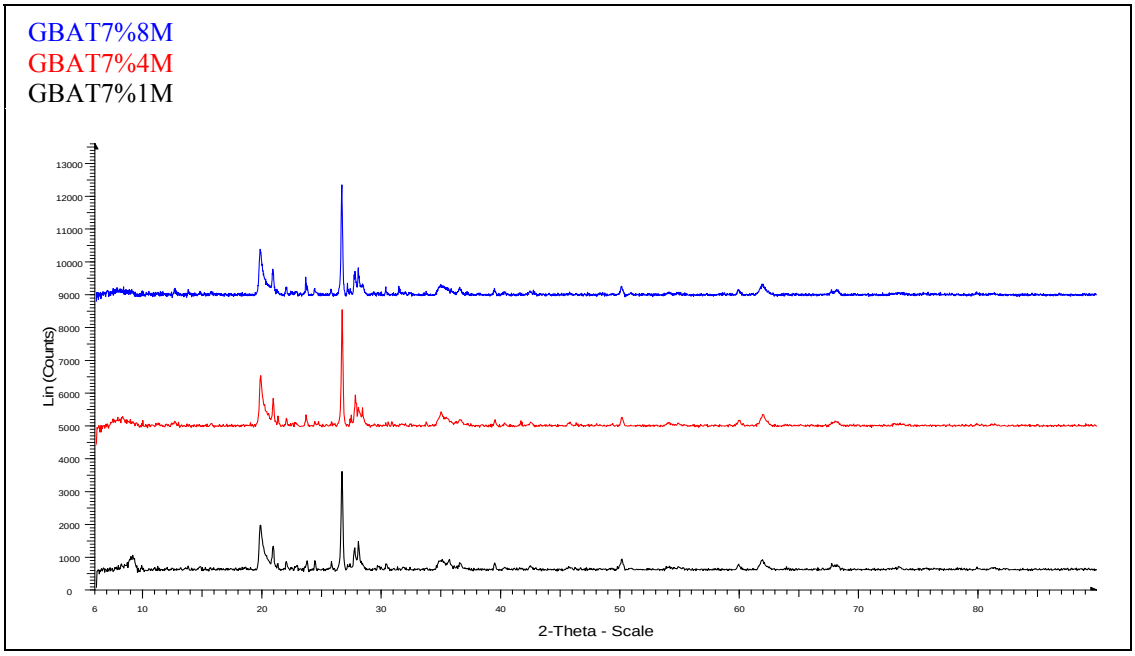
4.3.2 Micro-Structural Characterization

4.3.2.1 XRD Results

X-ray diffraction is a widely used primary investigative technique. This is because the method is easy and provides a great deal of rapidly interpretable information on many aspects of soil minerals. In this research, the technique was employed to assess the mineralogical changes induced by stabilizers on the soil structure and moreover, to detect the new crystalline compounds that are formed during the stabilization process.

XRD graphs of phosphoric acid and lime treated Bentonite soil after 1, 4, and 8 months of curing are shown in Figure 4.14. In addition, in order to compare the effect of acidic and basic stabilizers on soil's mineralogy, the XRD patterns of untreated and 8 months cured samples are presented in Figure 4.15. As can be seen, the major clay minerals present in the natural soil were montmorillonite ($2\theta \approx 8^o$, 21^o, 28^o, 35^o, 62^o) and illite ($2\theta \approx 9^o$, 22^o, 42^o) (Brown, 1961). Other reflections observed at approximately 22^o, 27^o, and 29.4^o 2θ corresponded to crystoballite, quartz, and calcite, respectively. The qualitative analysis of the XRD results indicated that in contrast to lime treatment, after application of the acid, the characteristic peaks of montmorillonite ($2\theta \approx 8^o$) and illite ($2\theta \approx 9^o$) appeared to have vanished. In addition, there was a slight decrease in the intensity of other peaks corresponding to these minerals. These alterations suggested that some sort of partial destruction in the structure of montmorillonite and illite minerals have occurred.

Comparison of the XRD patterns also revealed several new peaks at various 2θ angles. These peaks were observed at 30.7^o, 32^o, and 33.7^o 2θ for phosphoric acid and at 36.1^o and 49.3^o 2θ for lime treated samples. The peaks were tentatively assigned to aluminate phosphate hydrate and calcium silicate hydrate compounds in the phosphoric acid and lime treated samples, respectively (JCPDS, 1995).



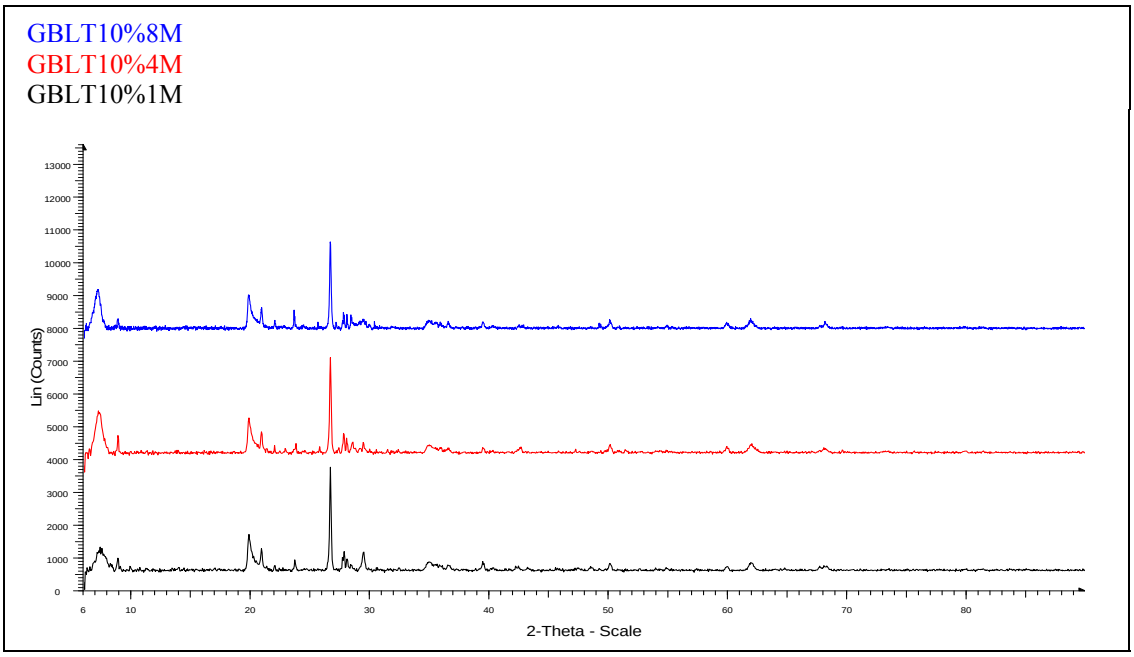


Figure 4.14 X-ray diffraction patterns for phosphoric acid and lime treated Green Bentonite after 1month, 4months, and 8months curing

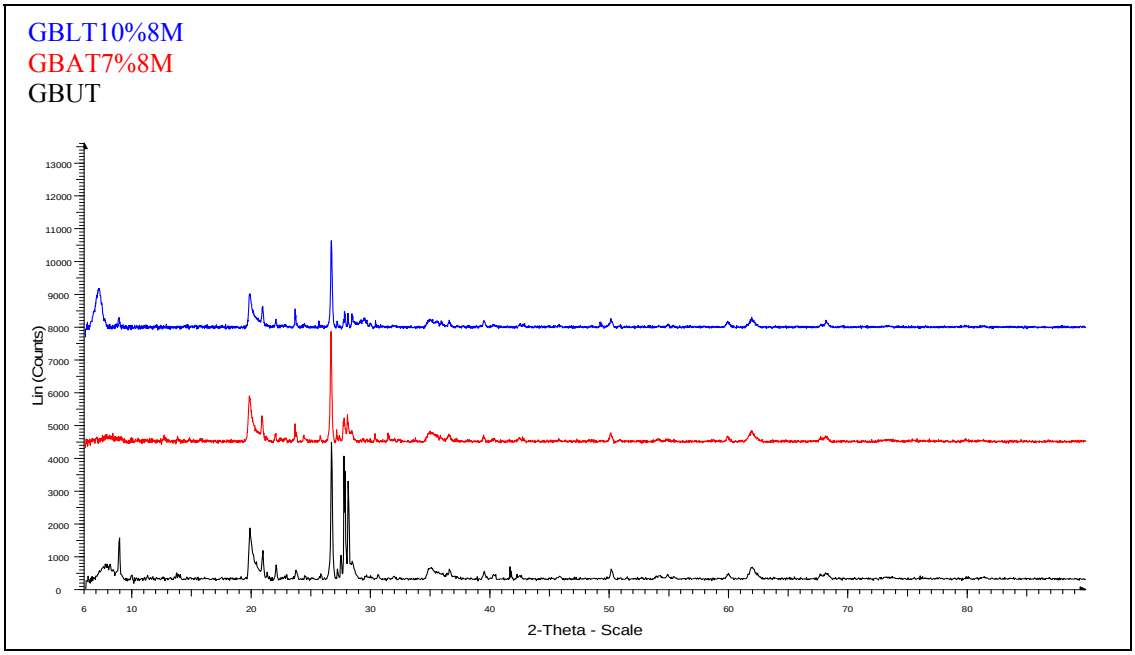


Figure 4.15 Comparison between X-ray diffraction patterns of natural, phosphoric acid, and lime treated Green Bentonite after 8 months period

X-ray diffraction patterns for untreated and chemically treated lateritic soil are illustrated in Figures 4.16 and 4.17, respectively. As can be seen in Figure 4.17, kaolinite ($2\theta \approx 12.5^{o}$, 18.5^{o}, 20^{o}, 36^{o}, 63^{o}), quartz ($2\theta \approx 21.5^{o}$, 25^{o}, 38^{o}), geothite ($2\theta \approx 18.2^{o}$, 21.8^{o}), and calcite ($2\theta \approx 29.4^{o}$, 43.2^{o}) were the major minerals present in the Laterite Clay samples (Brown, 1961). As indicated, with respect to the natural soil, no fundamental changes in the XRD patterns of acid and lime treated soil were observed. Nevertheless, there was a slight decrease in the intensity of peaks for kaolinite mineral. This was probably caused by the attack of stabilizers on mineral lattice. Furthermore, several new reflections regarding the formation of new products at various 2θ angles were evident. These peaks were observed at 14.2^{o}, 16.1^{o}, 27.2^{o}, 35^{o}, 54^{o}, 62.2^{o}, and 66^{o} 2θ for phosphoric acid and at 14.9^{o} and 16.7^{o} 2θ for lime treated samples. The former peaks were assigned to aluminate and iron phosphate hydrates and the latter to calcium aluminate hydrate compounds (JCPDS, 1995).

It must be noted that the intense peak observed at 13° 2θ angle for 7% lime treated samples after 1month curing was caused by the presence of feldspar in form of impurity and should be neglected from the results.

XRD graphs of phosphoric acid and lime treated White Kaolin after 1, 4, and 8 months of curing are shown in Figure 4.18. As evident from the natural soil (Figure 4.19), kaolinite mineral was identified by its strong diffraction lines at 12.5° and 25° 2θ angles (Brown, 1961). The peaks observed at approximately 9° and 18° corresponded to illite and gibbsite, respectively. Other reflections at approximately 21° and 27° implied the presence of quartz mineral. On the other hand, for chemically treated samples, all intensities of kaolinite mineral reflections decreased with time. Furthermore, in lime stabilized soil, a new reflection attributed to the formation of calcium aluminate hydrate (2θ ≈ 11.74°) was observed.

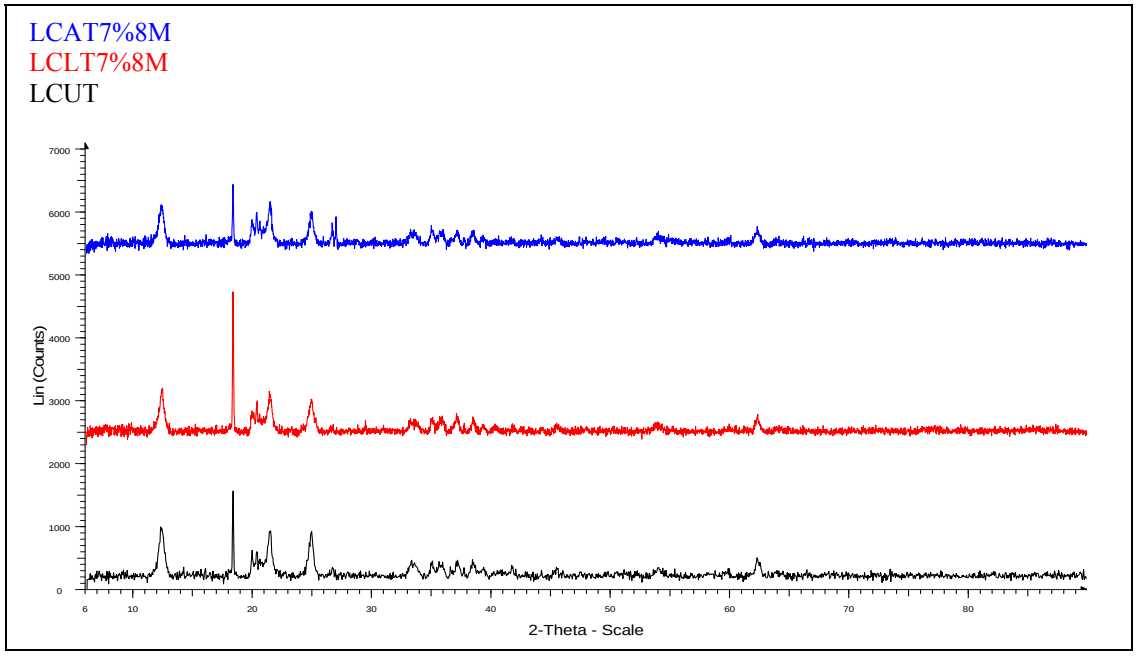
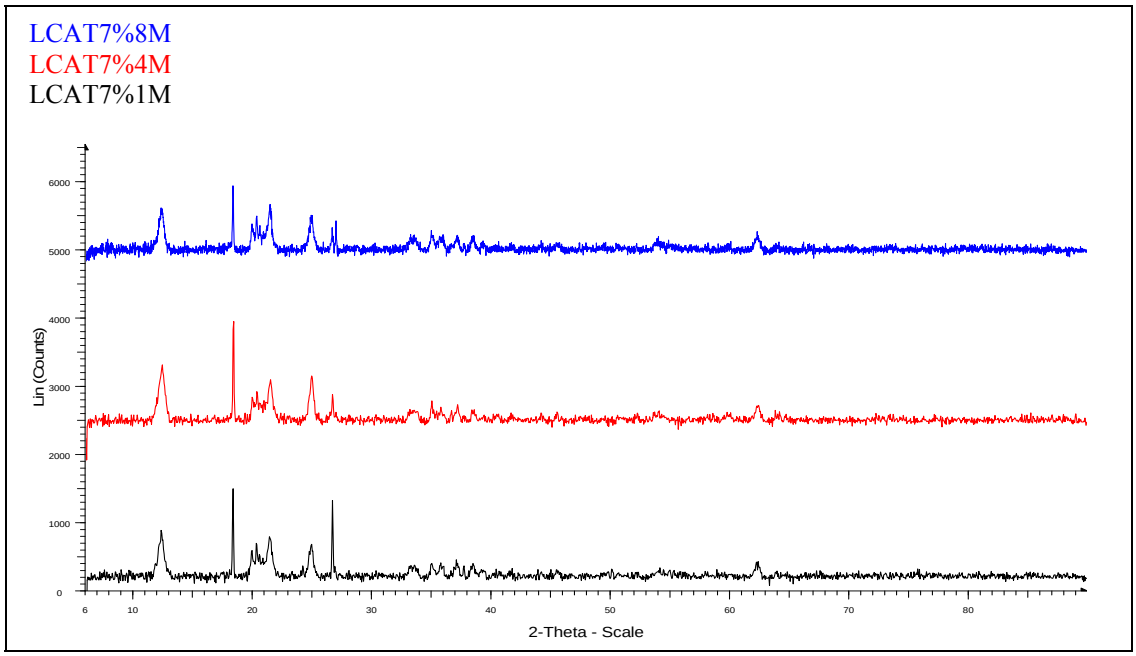


Figure 4.16 Comparison between X-ray diffraction patterns of natural, phosphoric acid, and lime treated Laterite Clay after 8 months curing period



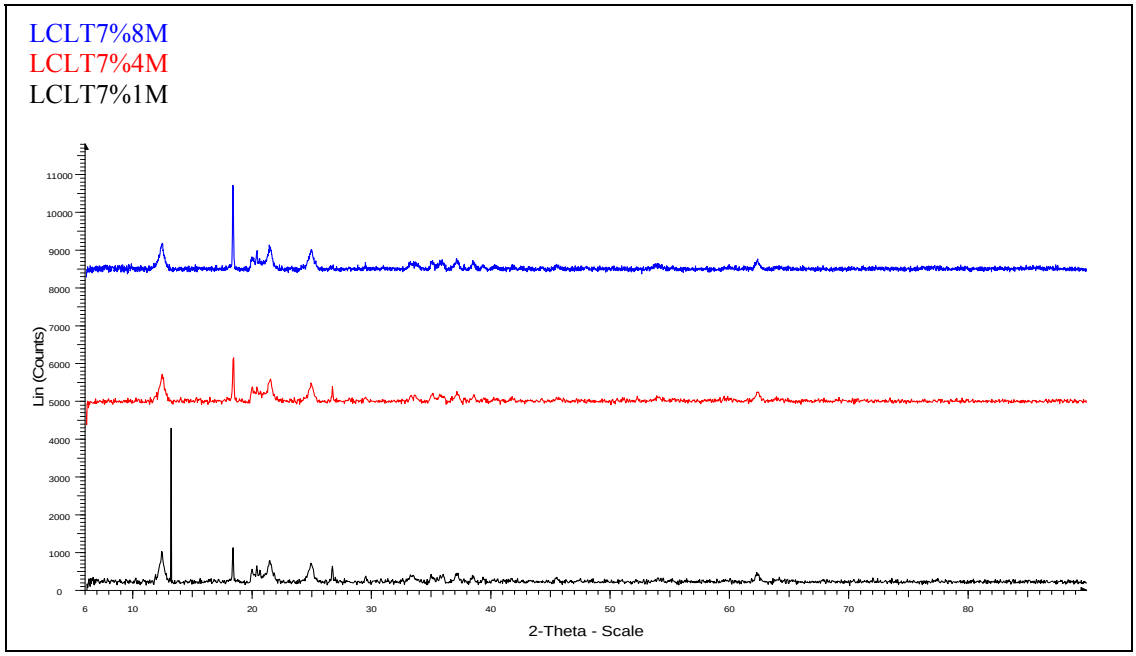


Figure 4.17 X-ray diffraction patterns for phosphoric acid and lime treated Laterite Clay after 1month, 4months, and 8months curing

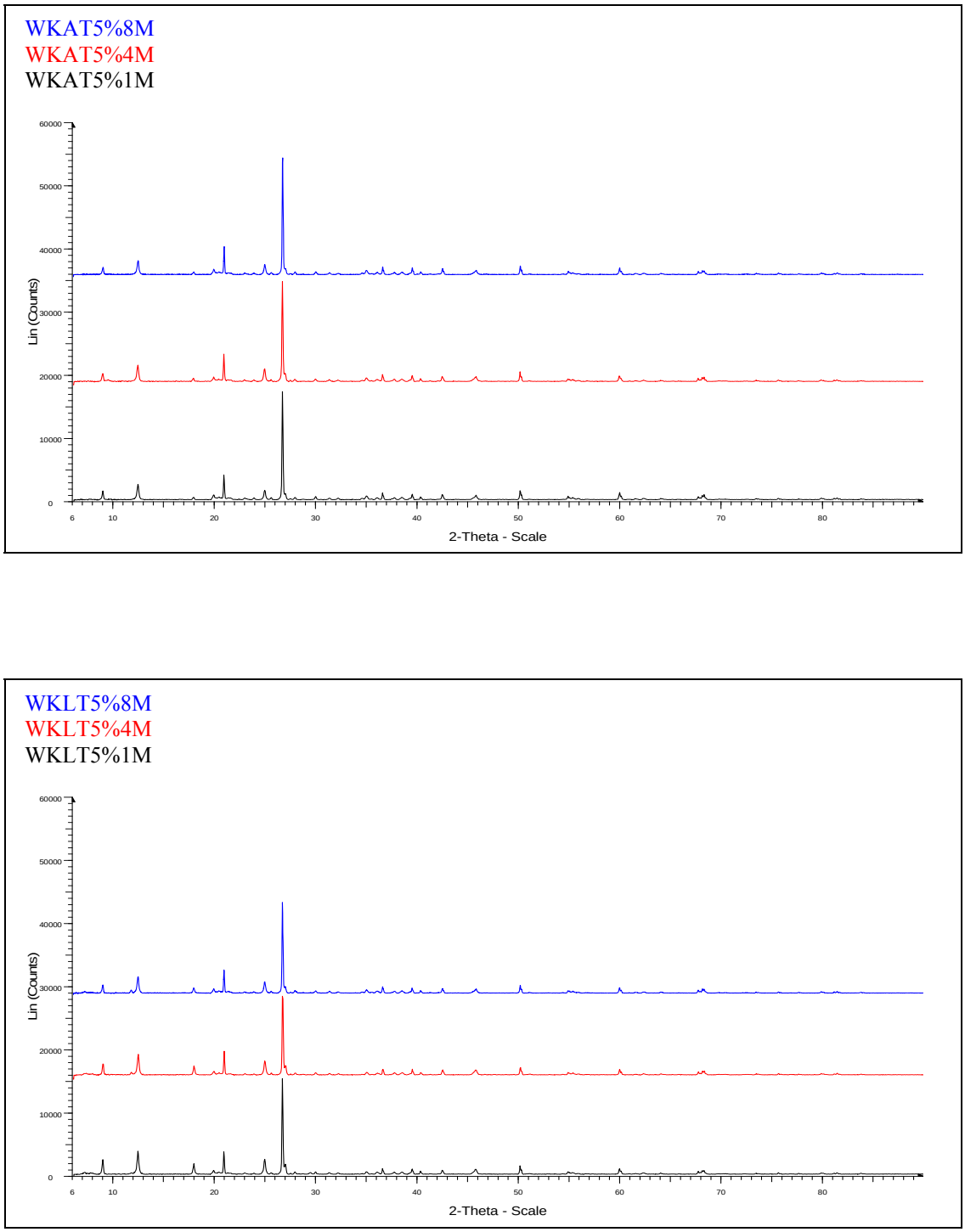


Figure 4.18 X-ray diffraction patterns for phosphoric acid and lime treated White Kaolin after 1month, 4months, and 8months curing

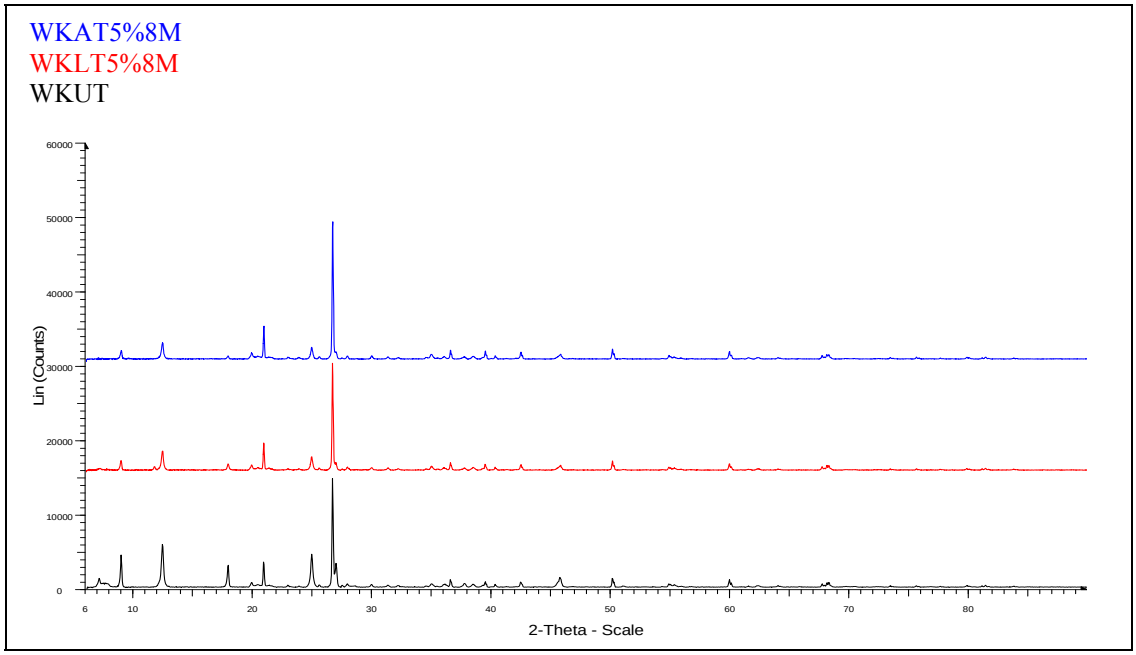
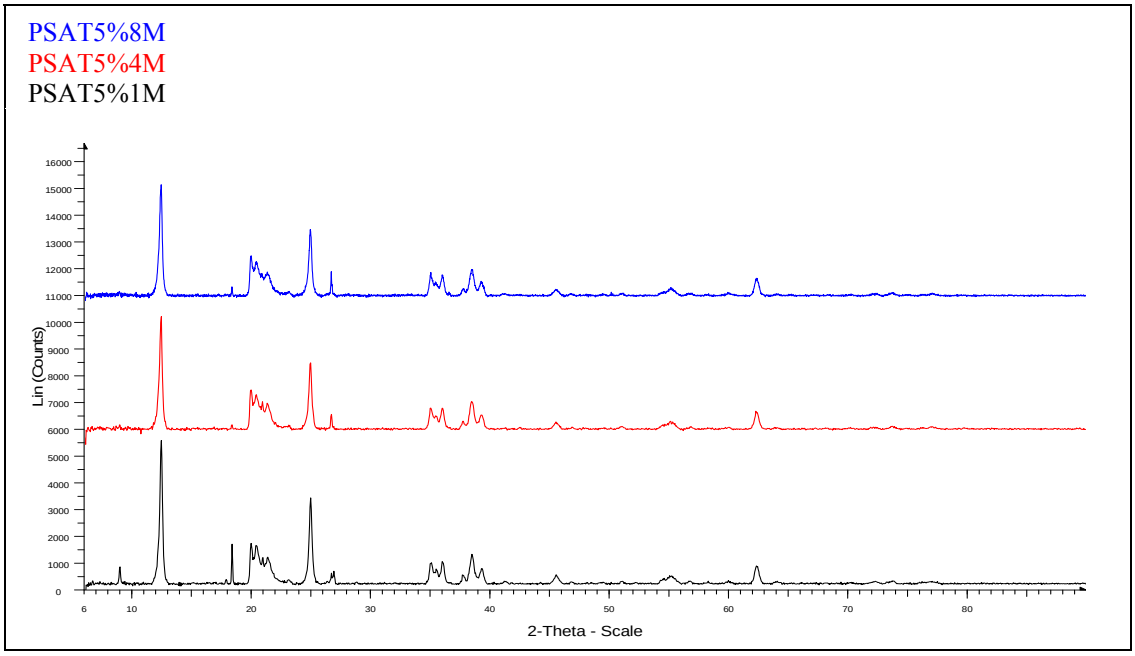


Figure 4.19 Comparison between X-ray diffraction patterns of natural, phosphoric acid, and lime treated White Kaolin after 8 months curing period

Figures 4.20 and 4.21 illustrate the XRD results for various Pink Soil mix designs. As can be seen, kaolinite (2θ ≈ 12.5°, 18.5°, 20°, 25°, 36°, 38.5°, 63°) was the dominant mineral present in the soil environment. Other reflections observed at approximately 18° and 27° 2θ corresponded to gibbsite and quartz, respectively. Comparison of the diffractograms of the treated samples with the reference untreated spectrum suggested that all intensities of clay mineral reflections decreased with time. Furthermore, new reflections at 18° and 58° 2θ for phosphoric acid and at 14°, 21°, 30°, and 42.5° 2θ for lime treated samples were observed. These peaks indicated the formation of phosphate and calcium aluminate hydrate compounds in the acid and lime treated samples, respectively (JCPDS, 1995).



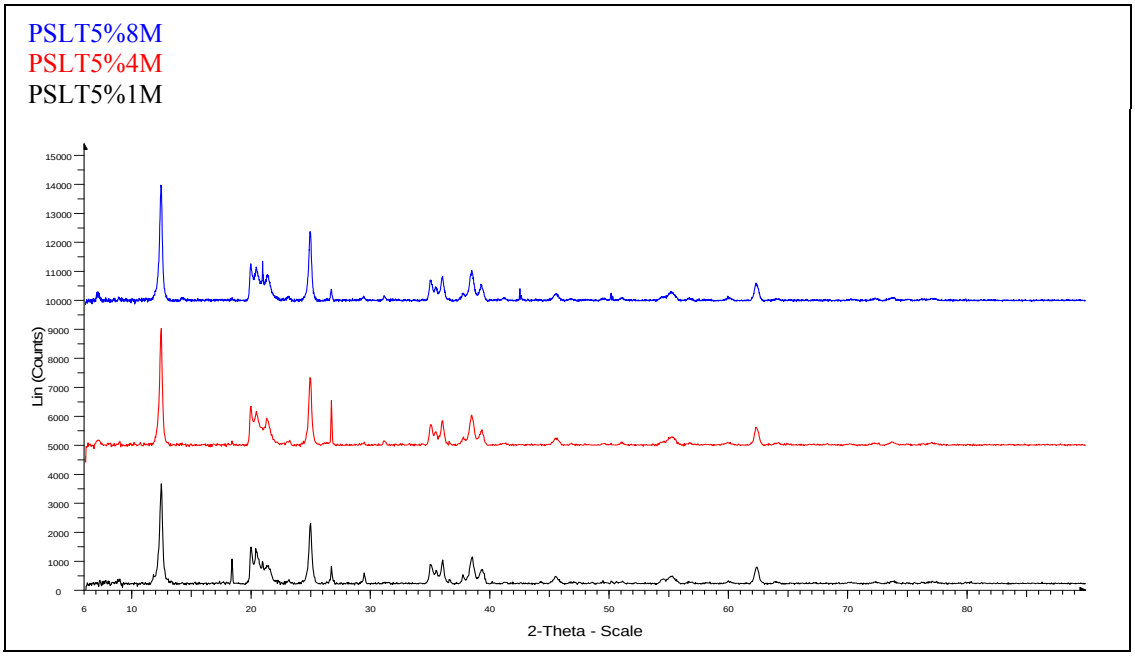


Figure 4.20 X-ray diffraction patterns for phosphoric acid and lime treated Pink Soil after 1month, 4months, and 8months curing

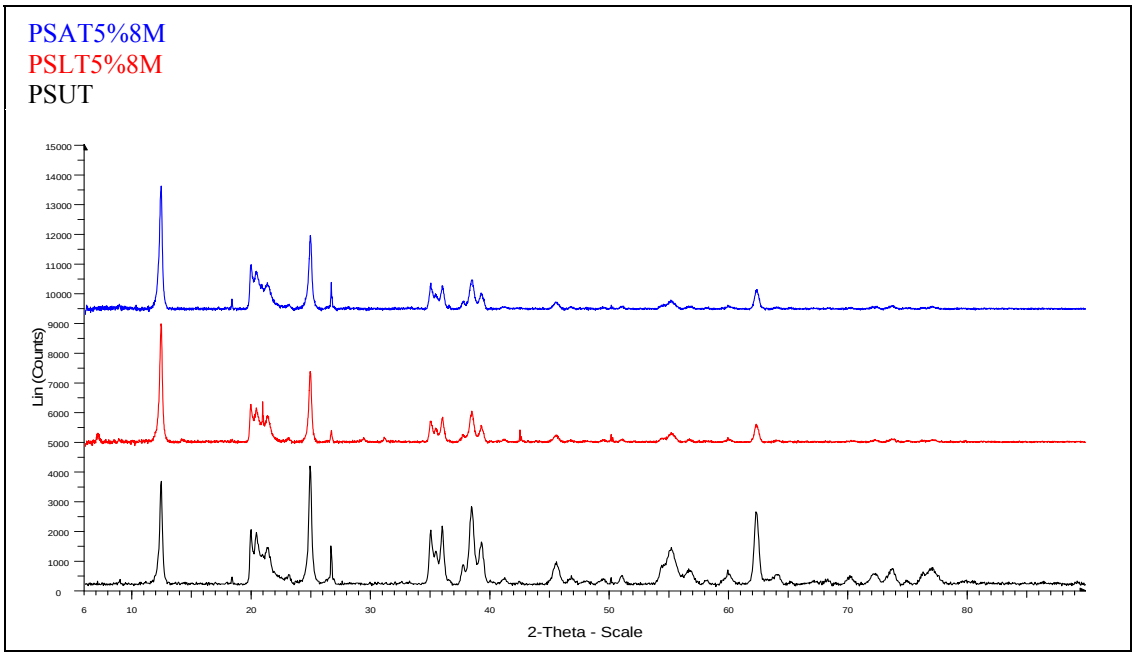


Figure 4.21 Comparison between X-ray diffraction patterns of natural, phosphoric acid, and lime treated Pink Soil after 8 months curing period

4.3.2.2 EDAX Results

In this thesis, energy dispersive x-ray spectrometry was carried out in order to identify the elements present on the surface of clay particles. Also the intensity of peaks at various time intervals was used to monitor the relative elemental changes induced by the stabilizers. EDAX spectrums of the untreated and 8 months cured Green Bentonite specimens containing 7% phosphoric acid and 10% lime are shown in Figure 4.22 (refer to **Appendix B** for samples of data obtained from EDAX analysis). In addition, the Al:Si, Ca:Si, and P:Si ratios for different mix designs are presented in Table 4.3. As can be seen, aluminum (Al), silicon (Si), magnesium (Mg), sodium (Na), iron (Fe), and calcium (Ca) peaks were clearly evident in both the untreated and treated samples with the latter showing much greater intensity for the lime treatment. The presence of these elements along with their intensity confirmed the dominancy of montmorillonite mineral in the soil medium (Carroll and Starkey, 197l). In addition, the acid treated samples also contained phosphorous (P).

The presence of phosphorous was consistent with the application of phosphoric acid to the soil medium. It should be mentioned that the traces of sulfur (S) found in the spectrums of treated samples were probably introduced by the chemical stabilizers.

Comparison of the EDAX results for the Al:Si ratio of untreated, phosphoric acid and lime treated Bentonite samples did not yield significant changes with curing time. Nonetheless, there was a higher reduction in the Al:Si ratio of acid treated samples after 8 months curing. This was consistent with the higher extraction of alumina from the clay mineral structure. Furthermore, the results demonstrated in Table 4.3 revealed some interesting points regarding the surface composition of clay particles. As can be seen for the acid and lime stabilized soils, the P:Si and Ca:Si ratios increased significantly in comparison to the natural soil, with the ratios reaching a maximum after 4 months of curing. This behavior can be attributed to the development of a gel compound micro-structure containing stabilizer ion on the surface of clay particles. In addition, the considerable release of silica in lime treated samples contributed to a much higher Ca:Si ratio. On the other hand, after 8 months of curing, the P:Si and Ca:Si ratios showed a relatively lower value. This was probably due to the crystallization of cementitious reaction products into the pores of mineral particles and/or an increase in the sources of silica exposed at the surface of clay particles.

The time-dependent changes in the Al:Si, Ca:Si, and P:Si ratios of Laterite mix designs are shown in Table 4.4. In addition, EDAX spectrums corresponding to the natural and 7% phosphoric acid and lime treated soil are presented in Figure 4.23. As apparent, high intensities of silicon (Si), aluminum (Al), phosphorus (P), and iron (Fe) peaks were observed in all samples. The concentration of these elements and in particular the iron element confirmed the lateritic nature of the soil and moreover the presence of free iron oxides on the surface of clay particles (Carroll and Starkey, 197l). In addition, the lime treated samples also contained calcium (Ca). The presence of calcium was consistent with the application of lime to the soil environment. It should be noted that the high intensities of Platinum (Pt) peak was due to the thickness of coating which was taken into consideration in determining the Al/Si, Ca/Si, and P/Si ratios.

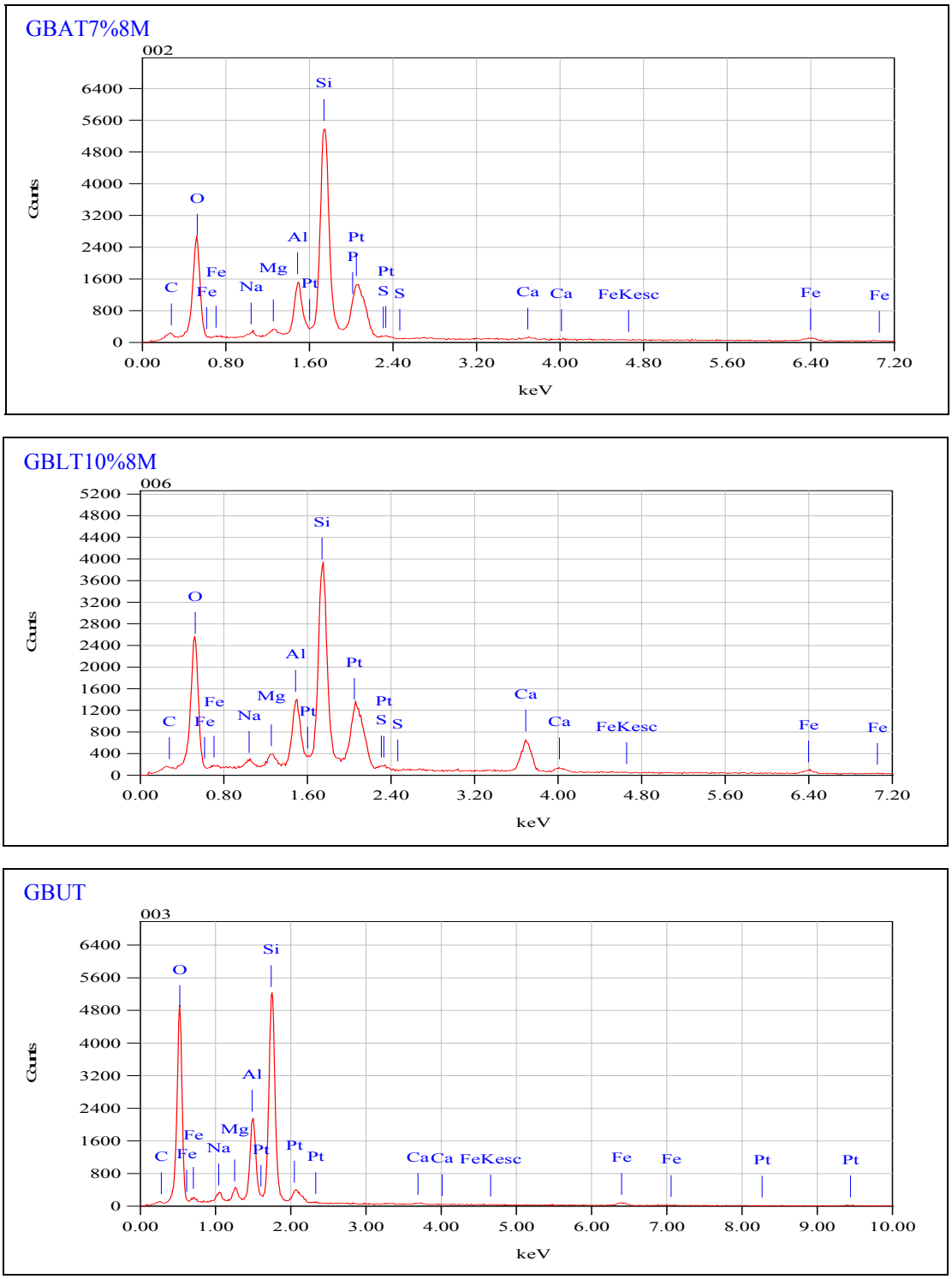


Figure 4.22 EDAX spectrums of untreated, lime and phosphoric acid treated Green Bentonite after 8months curing time

Table 4.3 : Variation of Al:Si, Ca:Si, and P:Si ratios for various Green Bentonite mix designs with curing time

Sample Description		Ratio (wt %)		
Mix Design	Curing Time (Months)	Al:Si	Ca:Si	P:Si
GBUT	-	0.35	0.02	0.00
GBAT7%	1	0.35	0.04	0.17
GBLT10%	1	0.33	0.28	0.00
GBAT7%	4	0.33	0.03	0.24
GBLT10%	4	0.30	0.53	0.00
GBAT7%	8	0.27	0.02	0.16
GBLT10%	8	0.30	0.35	0.00
Note: GB: Green Bentonite; LT: Lime Treated; AT: Acid Treated; UT: Untreated.				

As shown in Table 4.4, for all design mixes, the Al:Si ratio varied less than 10% between the untreated and treated samples. These results suggested that the soil structure did not change significantly following the treatment. However, as indicated by the P:Si and Ca:Si ratios, there were a appreciable change in the surface composition of clay particles. As can be seen for the acid treated mixes, the P:Si ratio decreased significantly after 4 months of curing. This behavior suggested an increase in the sources of silica present at the surface of clay particles due to the dissolution of the coating. This was also believed to be the main cause of reduction in the Ca:Si ratio of lime treated samples from 0.94 to 0.34 on increasing the curing period from 1 to 8 months. On the other hand, at 8 months time interval, the P:Si ratio showed a relatively higher value. This was tentatively caused by the formation of a gel-like phosphate hydrate compounds on the surface of clay particles.

Table 4.4 : Variation of Al:Si, Ca:Si, and P:Si ratios for various Laterite Clay mix designs with curing time

Sample Description		Ratio (wt %)		
Mix Design	Curing Time (Months)	Al:Si	Ca:Si	P:Si
LCUT	-	1.13	0.00	0.77
LCAT7%	1	1.22	0.00	0.55
LCLT7%	1	1.05	0.94	0.58
LCAT7%	4	1.10	0.00	0.46
LCLT7%	4	1.12	0.66	0.47
LCAT7%	8	1.12	0.00	0.72
LCLT7%	8	1.21	0.39	1.00
Note: LC: Laterite Clay; LT: Lime Treated; AT: Acid Treated; UT: Untreated.				

EDAX spectra for untreated and chemically treated White Kaolin samples along with their corresponding Al/Si, Ca/Si, and P/Si ratios are presented in Figure 4.24 and Table 4.5, respectively.

As seen in the spectrums, high intensities of aluminum (Al), silicon (Si), and phosphorus (P) followed by lower levels of iron (Fe), magnesium (Mg), sulfur (S), and potassium (K) were evident. The presence and intensity of these elements was in good agreement with kaolinite minerals chemical composition (Carroll and Starkey, 197l). As shown in Table 4.5, there were considerable changes in the Al:Si ratio of the stabilized samples. The increase in the Al:Si ratio of the treated samples after 4 months of curing time was consistent with a mechanism in which compounds of aluminate hydrate gels are deposited on the surface of clay particles. On the other hand, after 8 months of curing, the Al:Si ratio showed a relatively lower value. This was because of an increase in the sources of silica present at the surface of 1:1 silica:alumina structured kaolinite particles. This was also believed to be the main cause of decrease in the Ca:Si and P:Si ratios of treated samples with curing time.

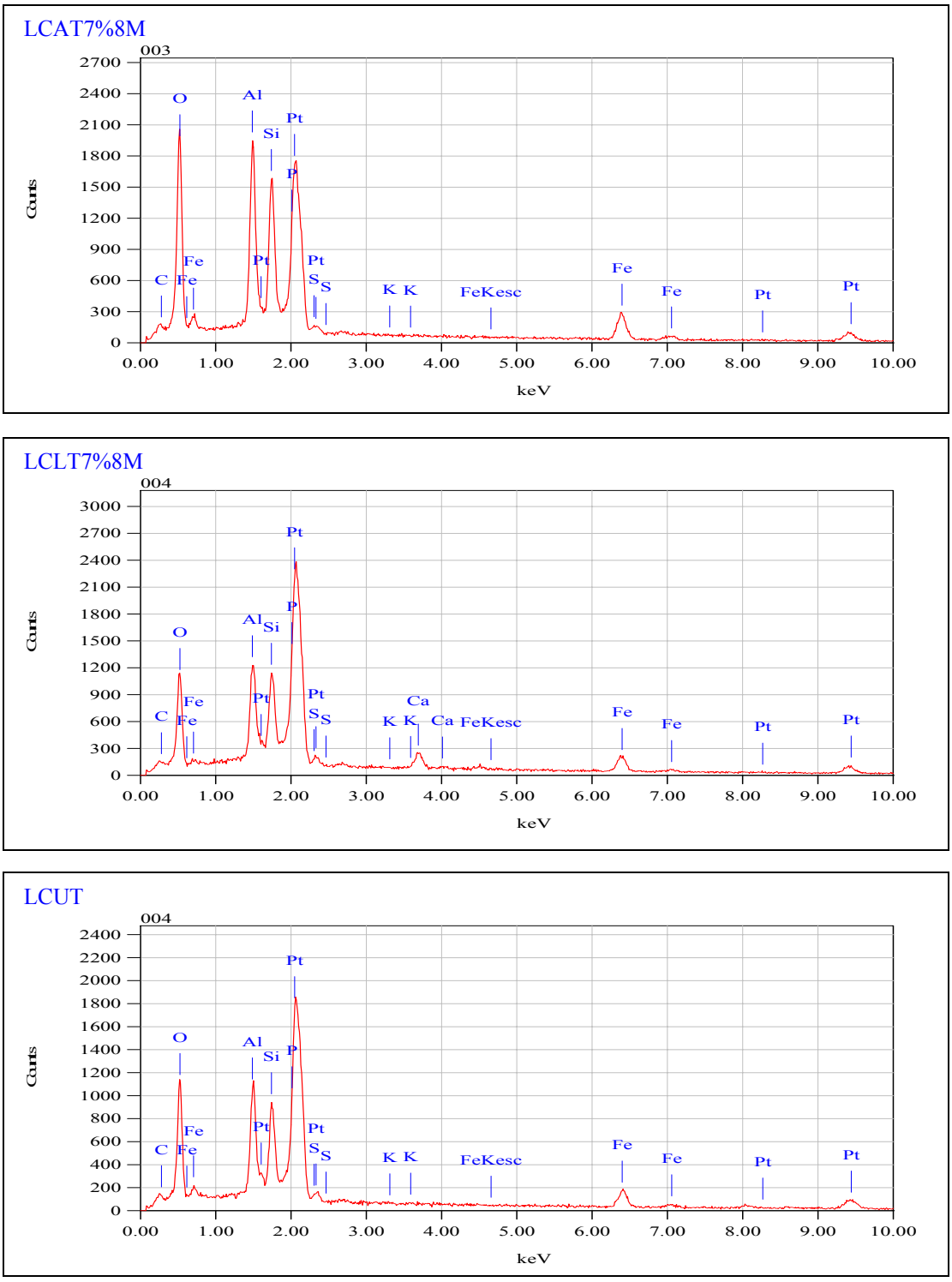


Figure 4.23 EDAX spectrums of untreated, lime and phosphoric acid treated Laterite Clay after 8months curing time

Table 4.5 : Variation of Al:Si, Ca:Si, and P:Si ratios for various White Kaolin mix designs with curing time

Sample Description		Ratio (wt %)		
Mix Design	Curing Time (Months)	Al:Si	Ca:Si	P:Si
WKUT	-	0.63	0.00	0.19
WKAT5%	1	0.77	0.00	0.52
WKLT5%	1	0.70	0.21	0.17
WKAT5%	4	0.84	0.00	0.47
WKLT5%	4	0.75	0.20	0.11
WKAT5%	8	0.70	0.00	0.20
WKLT5%	8	0.55	0.07	0.20
Note: WK: White Kaolin; LT: Lime Treated; AT: Acid Treated; UT: Untreated.				

The variations in the Al:Si, Ca:Si, and P:Si ratios of Pink Soil mix designs are shown in Table 4.6. In addition, EDAX spectra corresponding to the natural and 5% phosphoric acid and lime treated samples are presented in Figure 4.25. As evident, high intensities of aluminum (Al), silicon (Si), and phosphorus (P) followed by lower levels of iron (Fe), copper (Cu), zinc (Zn), sulfur (S), and potassium (K) were observed in all samples. The lime treated samples also contained calcium (Ca).

As indicated by the P:Si and Ca:Si ratios in Table 4.6, for all design mixes, there was a appreciable change in the surface composition of soil particles which emphasized on the fact that some sort of chemical reactions were taking place. For instance, in phosphoric acid treated samples, the P:Si ratio more than doubled after 4 months of curing. This behavior suggested an increase in the amount of phosphate compounds present on the surface of clay particles.

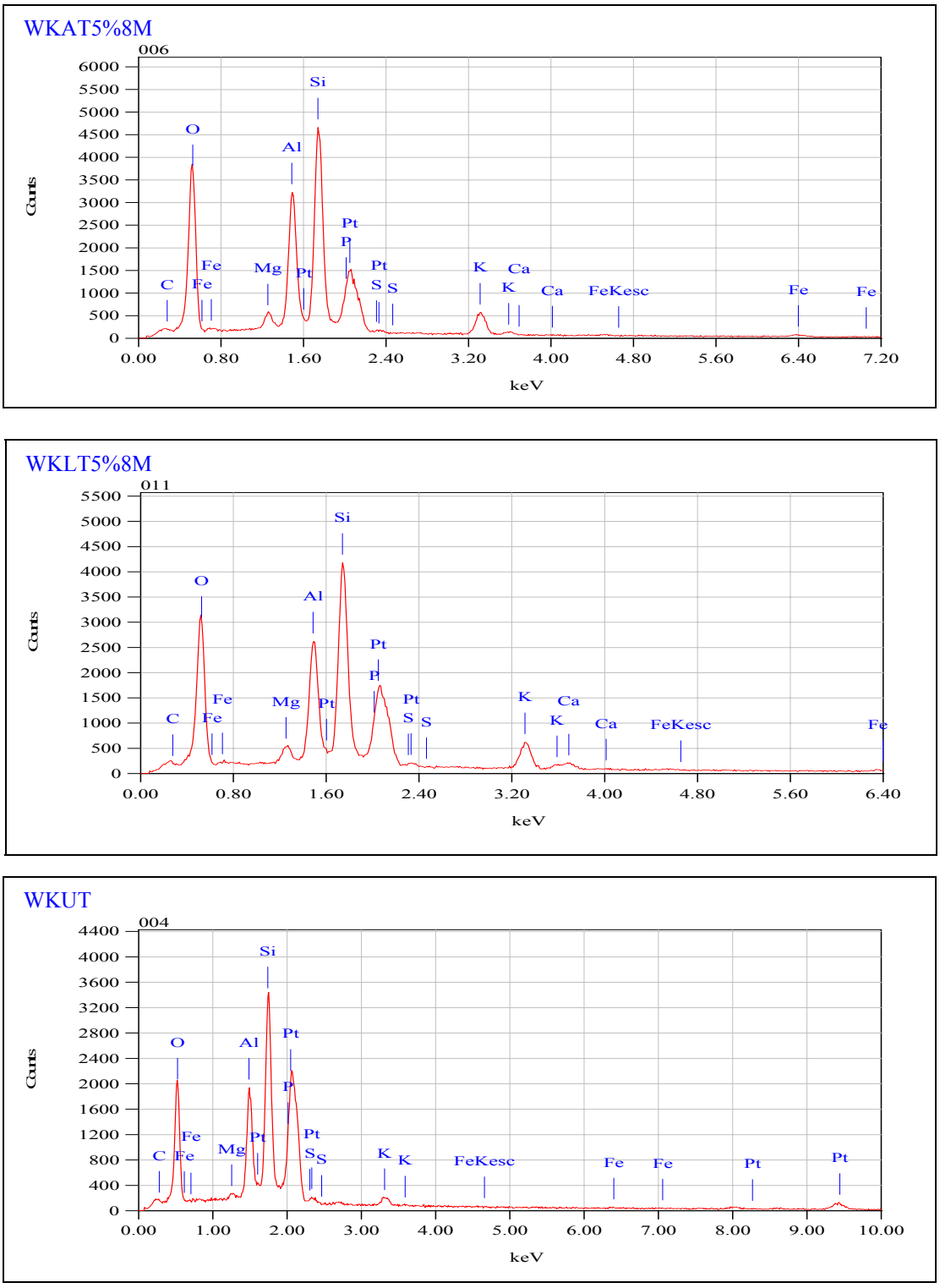


Figure 4.24 EDAX spectrums of untreated, lime and phosphoric acid treated White Kaolin after 8months curing time

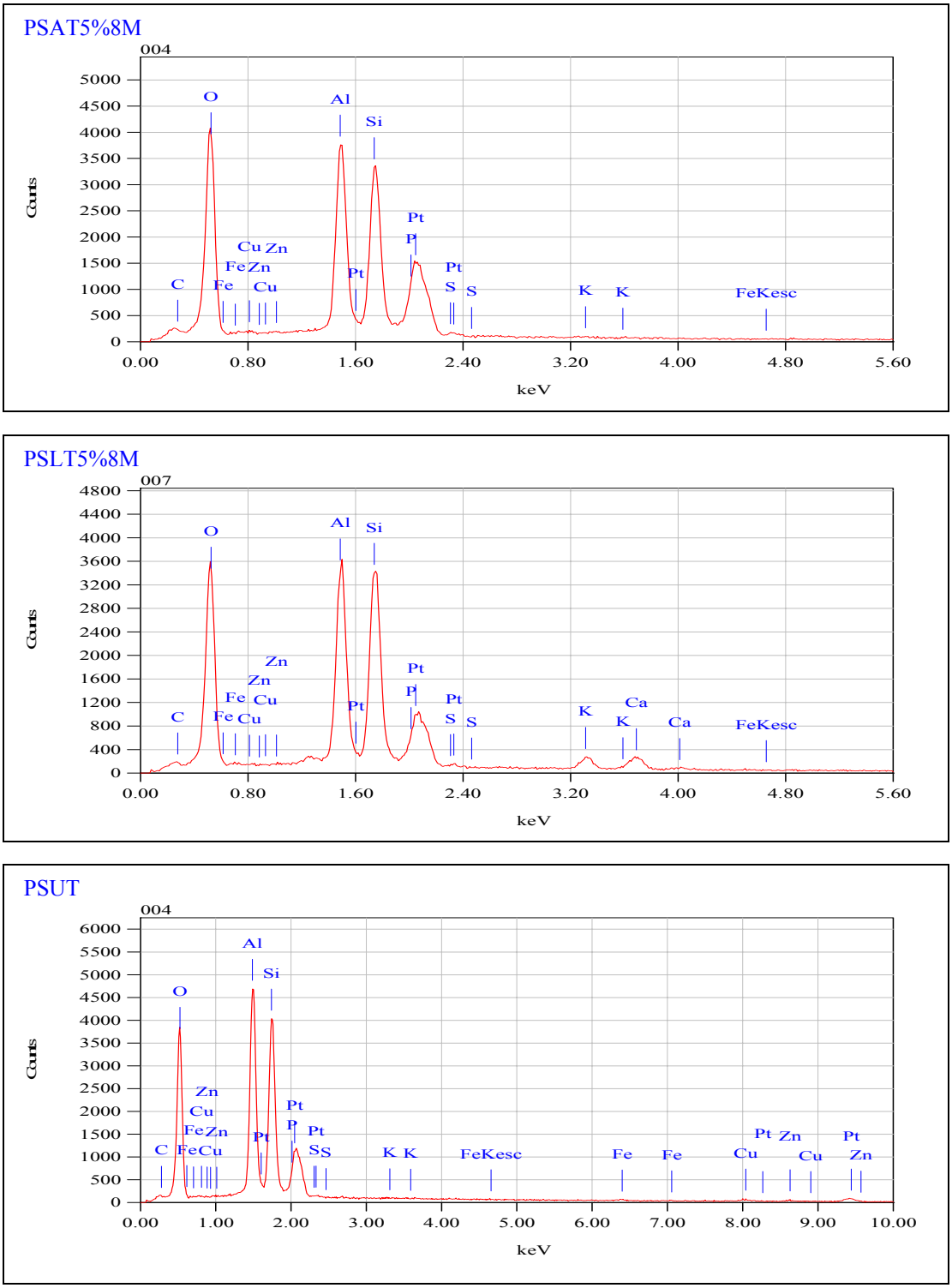


Figure 4.25 EDAX spectrums of untreated, lime and phosphoric acid treated Pink Soil after 8months curing time

Table 4.6 : Variation of Al:Si, Ca:Si, and P:Si ratios for various Pink Soil mix designs with curing time

Sample Description		Ratio (wt %)		
Mix Design	Curing Time (Months)	Al:Si	Ca:Si	P:Si
PSUT	-	0.83	0.00	0.12
PSAT5%	1	0.96	0.00	0.11
PSLT5%	1	0.96	0.18	0.10
PSAT5%	4	0.96	0.00	0.25
PSLT5%	4	0.98	0.26	0.15
PSAT5%	8	0.97	0.00	0.29
PSLT5%	8	0.81	0.13	0.14
Note: PS: Pink Soil; LT: Lime Treated; AT: Acid Treated; UT: Untreated.				

4.3.2.3 FESEM Results

With the exception of phosphoric acid stabilized soils, the use of electron microscopy in studying the morphological changes associated with lime treatment has been reported by many researchers (Willoughby *et al*., 1968; Rajasekaran and Narasimha Rao, 1997).

The micrograph of natural Green Bentonite is presented in Figure 4.26. As was expected, the untreated sample showed a dispersed film-like microstructure similar to that observed for montmorillonite mineral (Mitchell and Soga, 2005). In Figures 4.27 and 4.28, the morphology of phosphoric acid and lime treated Bentonite soil after 1month, 4months, and 8months of curing are shown. As can be seen, due to the chemical treatment the soil fabric has transformed from a flake based form into a more flocculated structure. In addition, the edges of clay particles seem to have been attacked. Furthermore, in 8 months cured samples, the presence of cementitious compounds in form of white lumps was evident. It should be stressed that by means of an energy dispersive x-ray spectrometer, these new phases with respect to phosphoric acid and lime treatment were roughly identified as Aluminate Phosphate Hydrate (APH) and Calcium Silicate Hydrate (CSH).

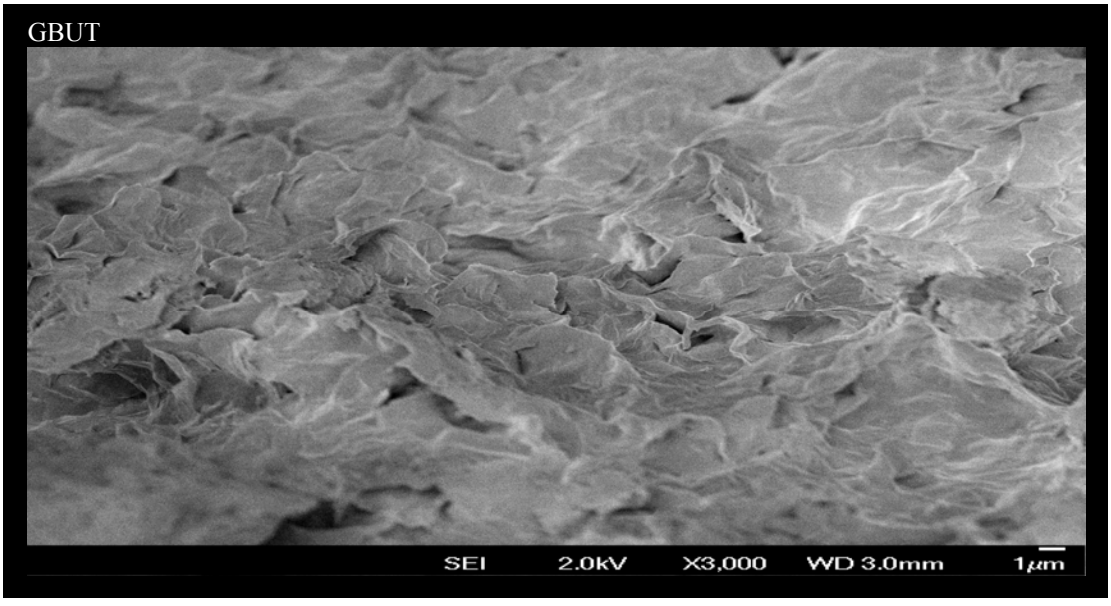


Figure 4.26 FESEM image of untreated Green Bentonite

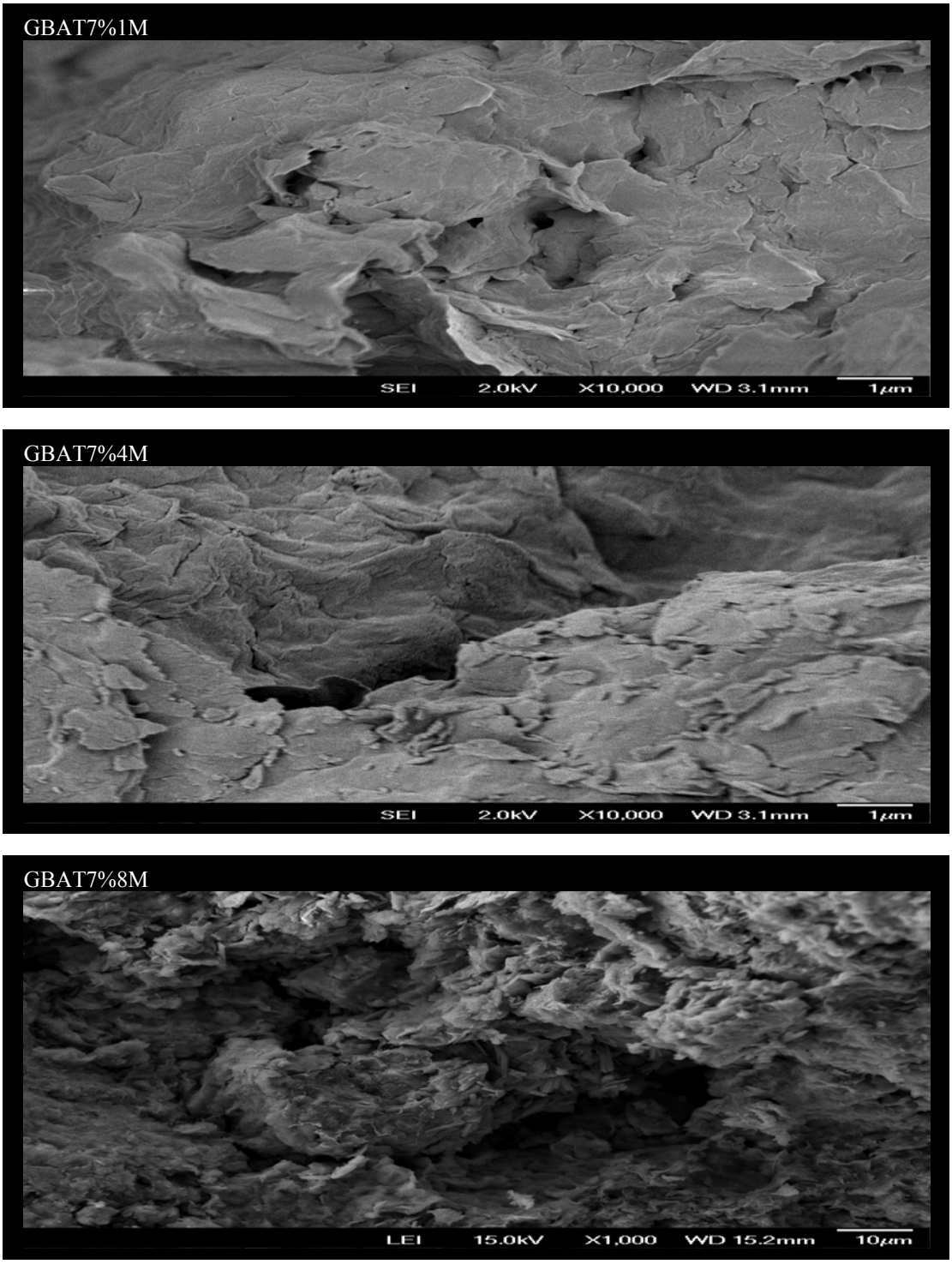


Figure 4.27 FESEM images of 7% phosphoric acid treated Green Bentonite after 1month, 4months, and 8months curing time

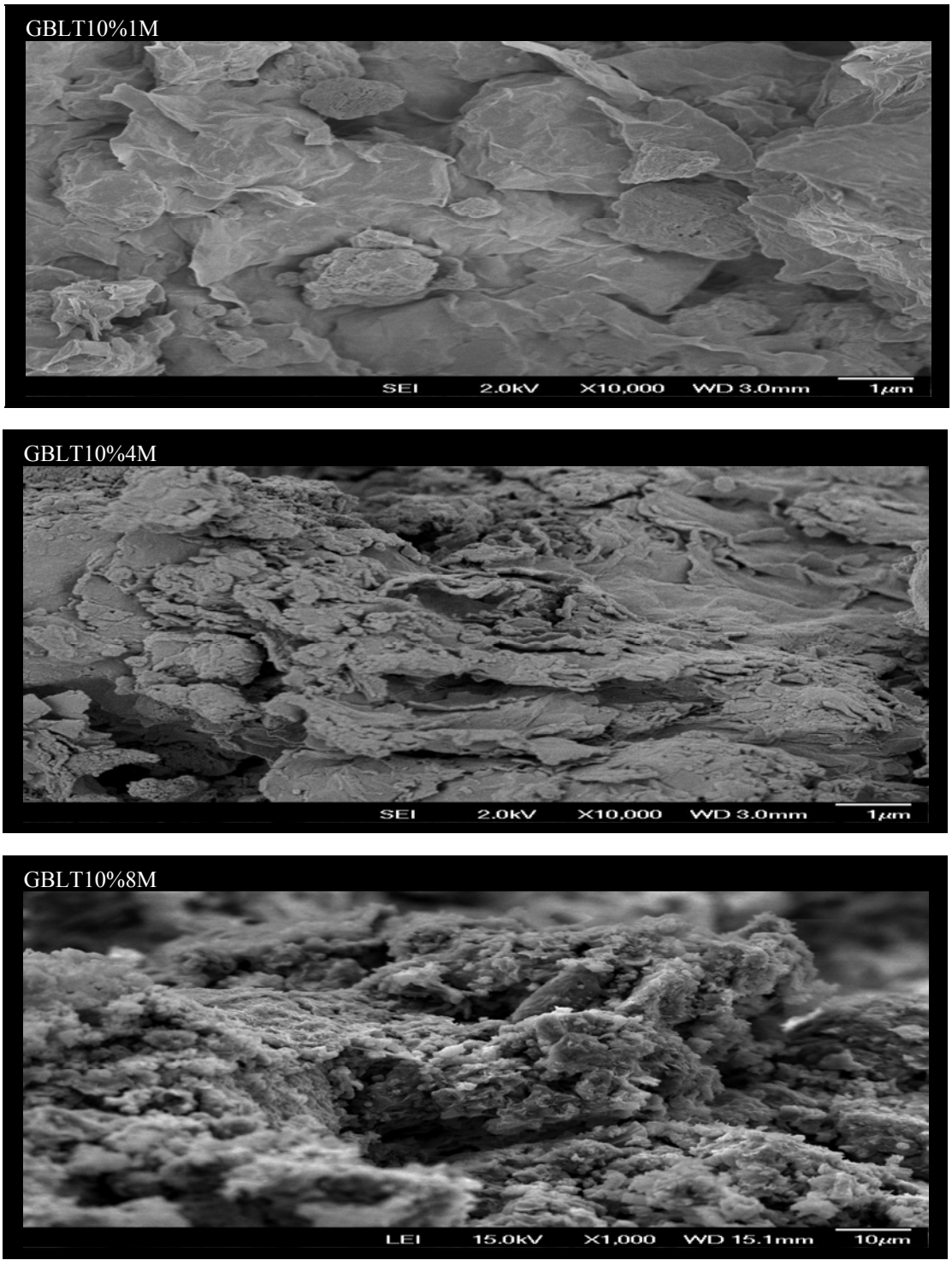


Figure 4.28 FESEM images of 10% lime treated Green Bentonite after 1month, 4months, and 8months curing time

Figure 4.29 refers to the micrograph of natural Laterite Clay. As can be seen, the free oxides present in the soil environment have coated and bonded the clay particles together.

In Figures 4.30 and 4.31, the morphology of phosphoric acid and lime treated samples at different time intervals are presented. It is apparent that at the early stages of curing, no appreciable changes in the texture of soil have occurred. However, after the 8 months curing period, the vigorous action of acid on soil particles and in particular the free oxides have transformed the soil structure into a more integrated composition consisting of sharper edged particles. On the other hand, in lime treated samples, the soil fabric revealed a more particle based microstructure. In addition, the formation of new compounds in form of white lumps was evident in both mix design.

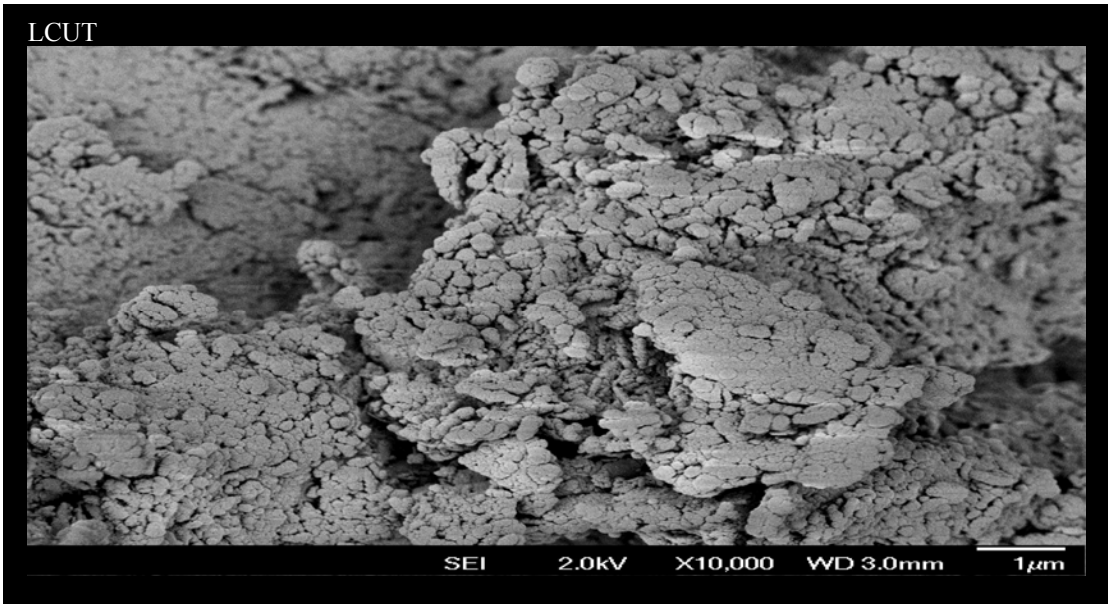


Figure 4.29 FESEM image of untreated Laterite Clay

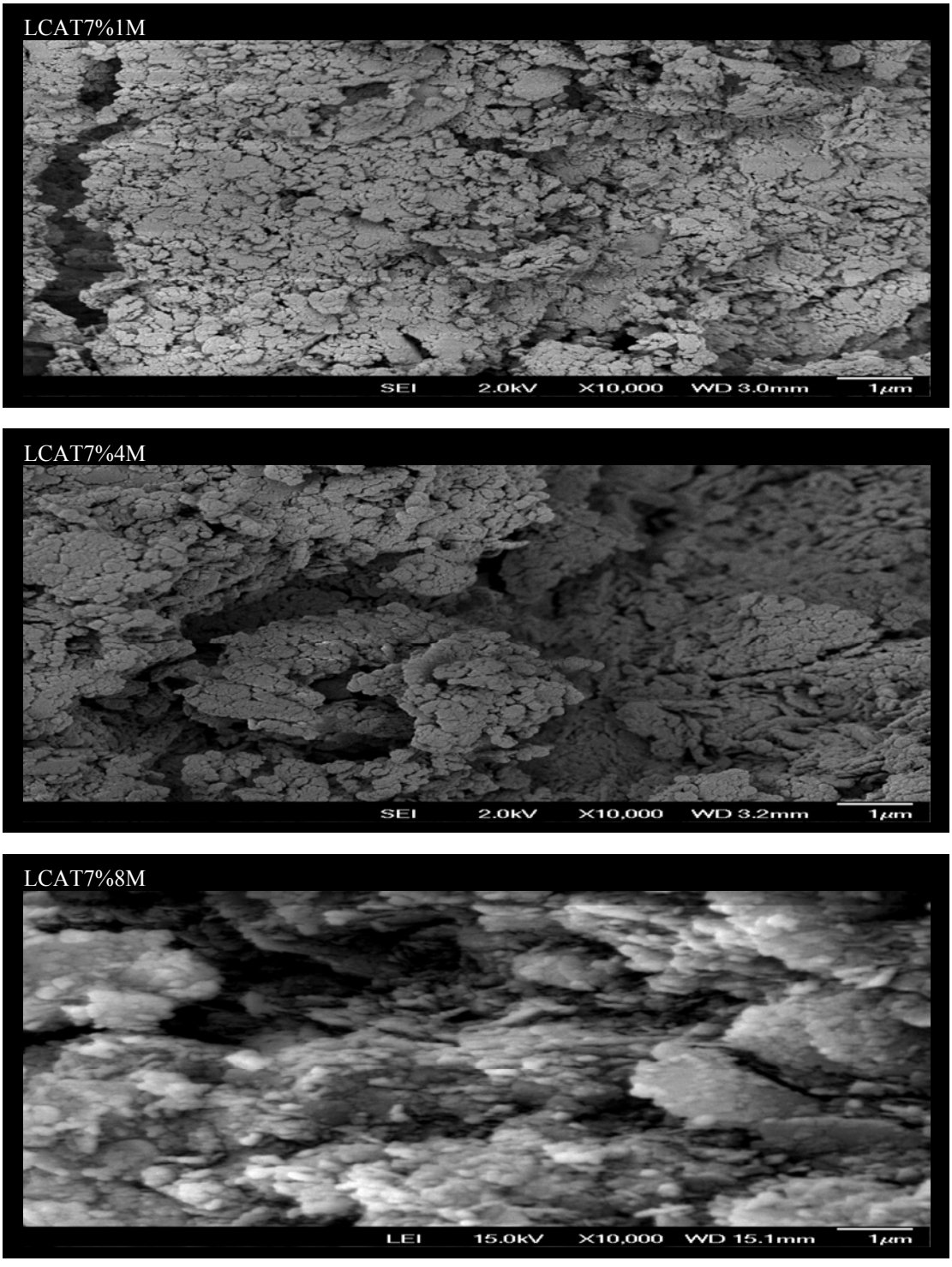


Figure 4.30 FESEM images of 7% phosphoric acid treated Laterite Clay after 1month, 4months, and 8months curing time

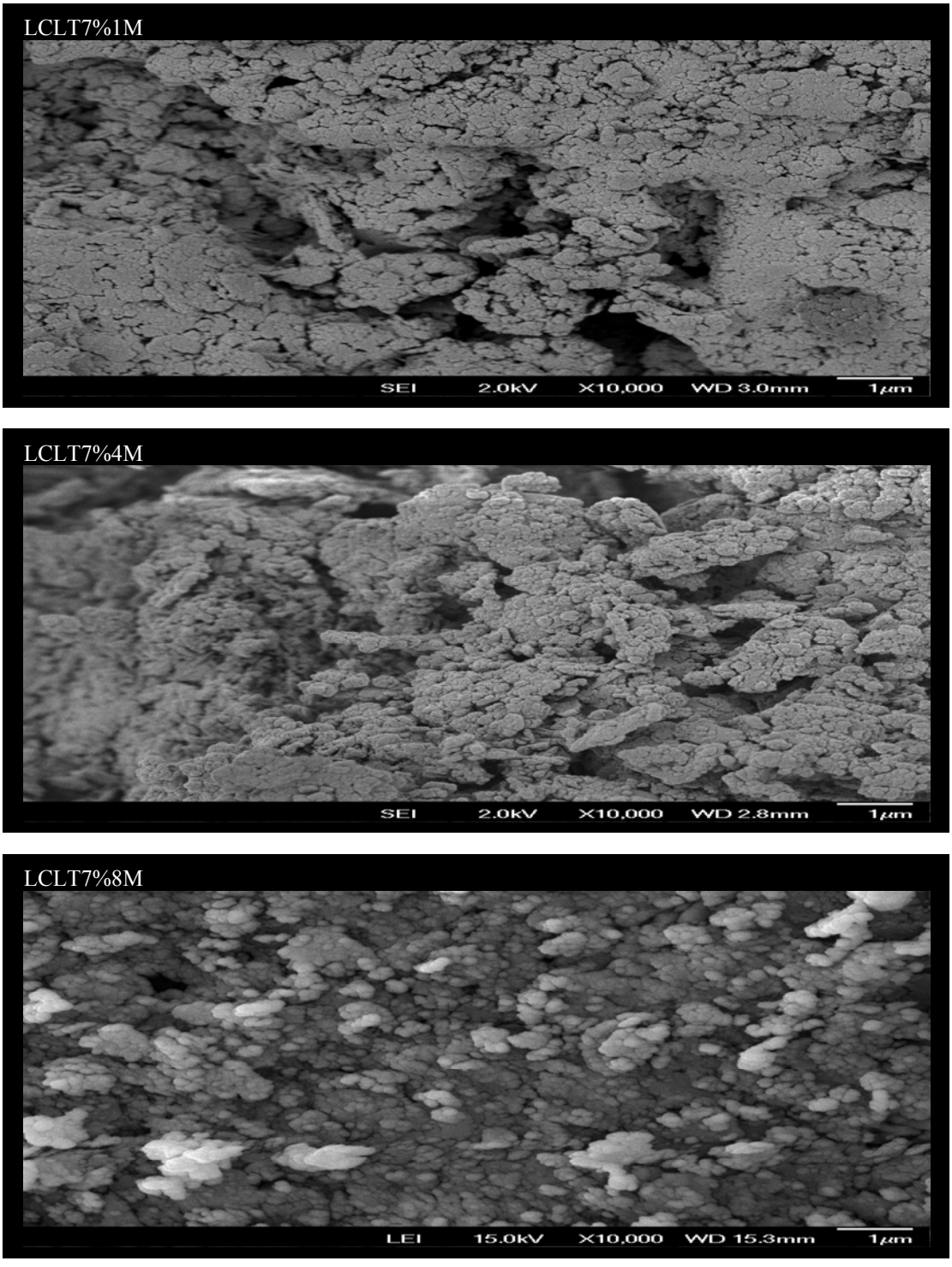


Figure 4.31 FESEM images of 7% lime treated Laterite Clay after 1month, 4months, and 8months curing time

FESEM images for untreated, phosphoric acid and lime treated White Kaolin soil are presented in Figures 4.32, 4.33, and 4.34, respectively. As shown, the neatly arranged book-like kaolinite particles were the predominant feature of the natural soil.

Comparison of the results indicated that the morphological changes seen in lime mix designs were similar to that observed in phosphoric acid treated samples but with a lesser intensity. In addition, in both mix designs, after 8 months of curing, the formation of white cementitious compounds on the surfaces of soil particles were apparent.

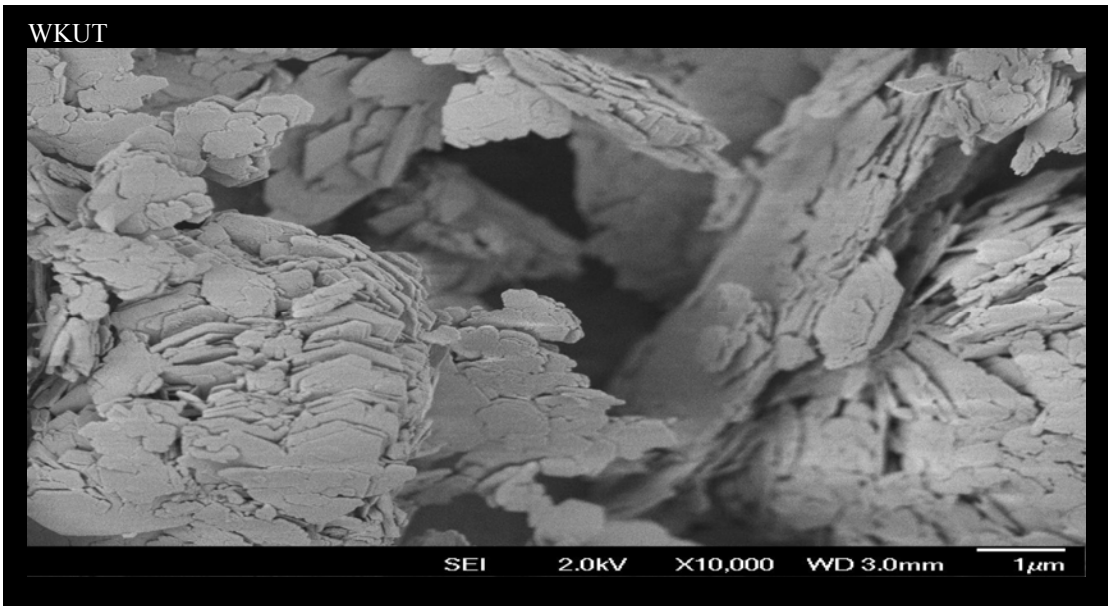


Figure 4.32 FESEM image of untreated White Kaolin

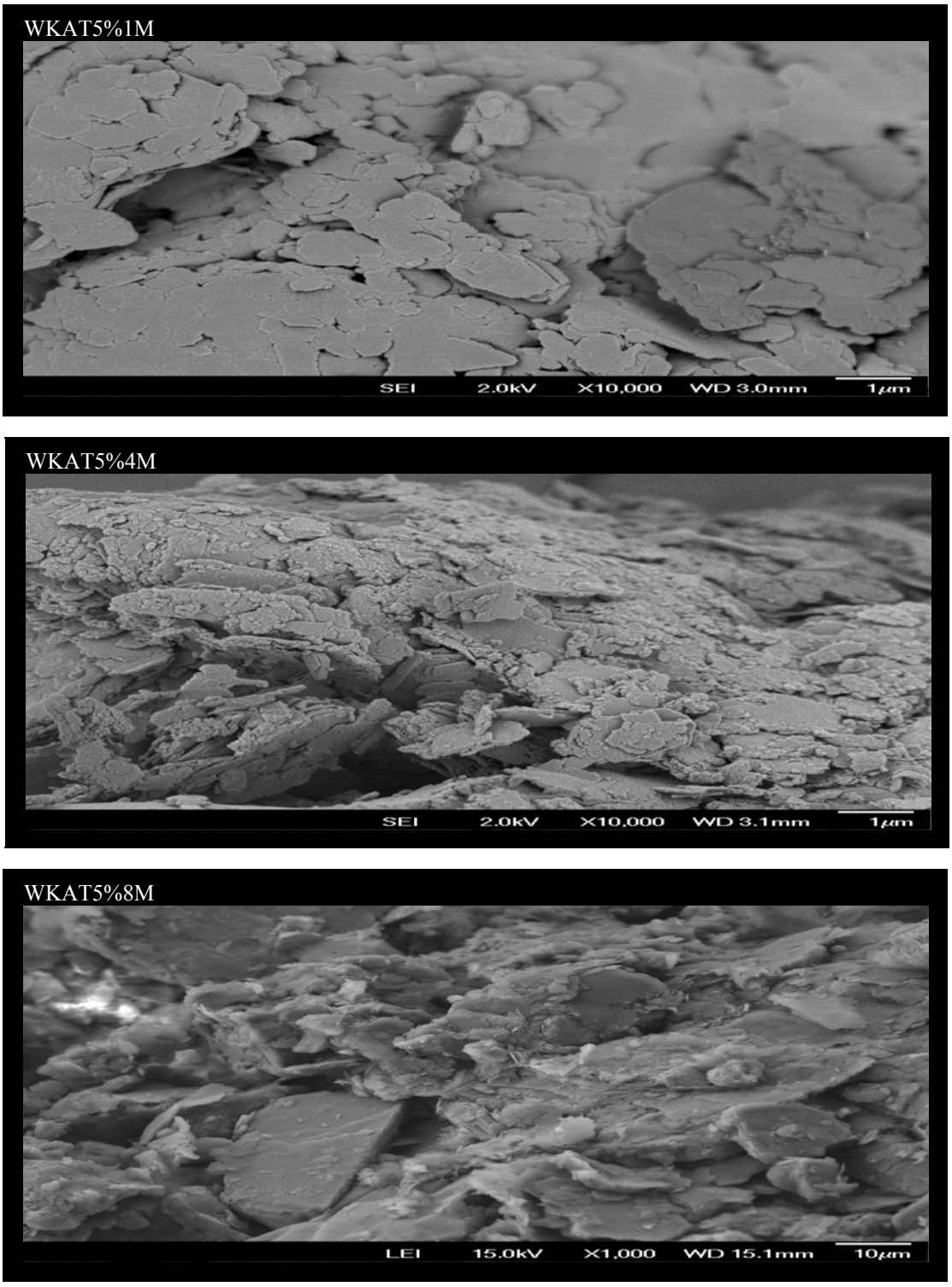


Figure 4.33 FESEM images of 5% phosphoric acid treated White Kaolin after 1month, 4months, and 8months curing time

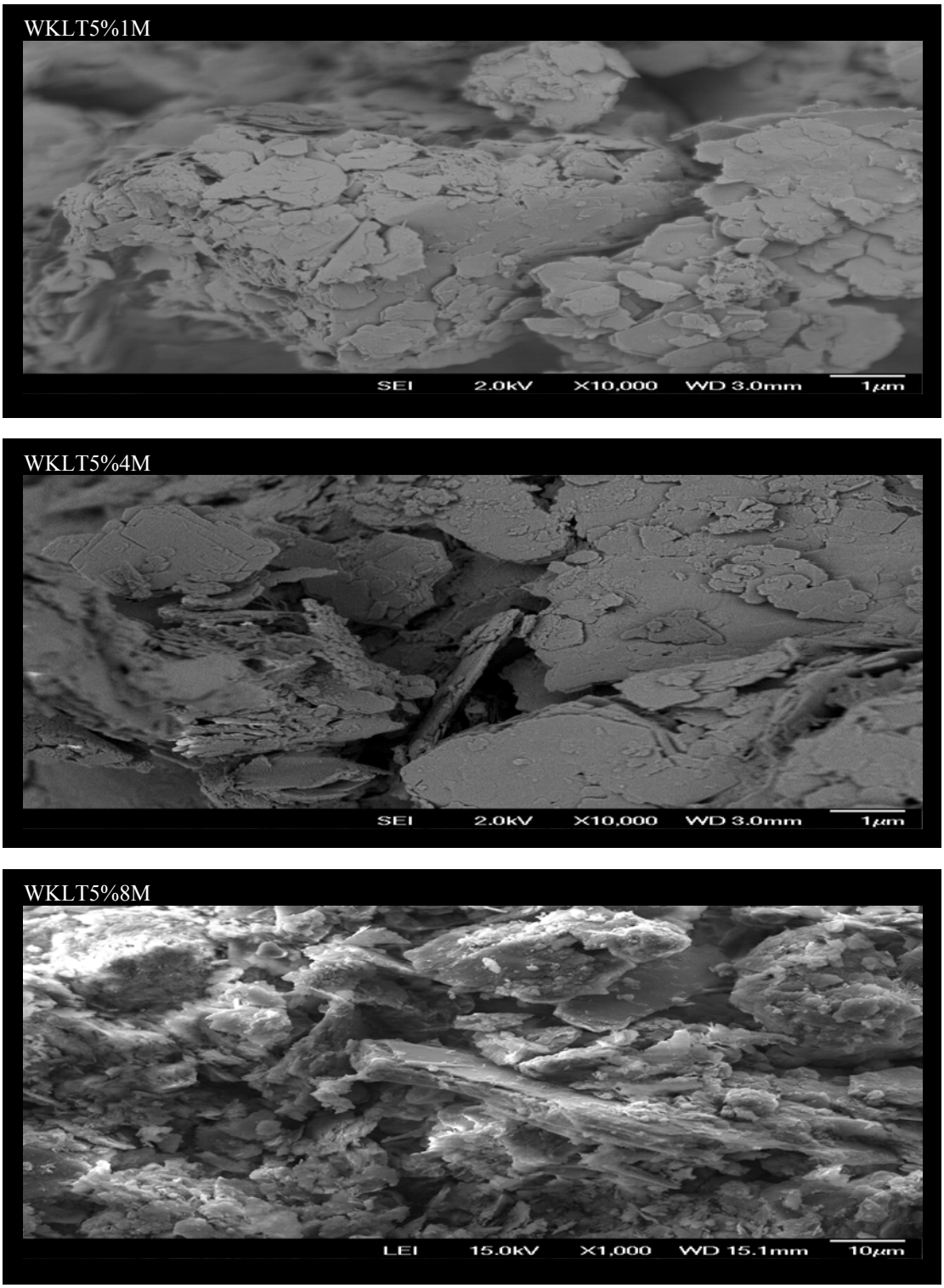


Figure 4.34 FESEM images of 5% lime treated White Kaolin after 1month, 4months, and 8months curing time

The FESEM results for untreated and treated Pink Soil samples are presented in Figures 4.35, 4.36, and 4.37, respectively. As can be seen, the presence of needle-like gypsum minerals in the soil medium was evident.

Evaluation of the FESEM images for lime and phosphoric acid mix designs indicated that after 8 of months curing, treated samples contained much lesser sharp fragments with a morphology completely different from the natural soil which was covered by large continuous gypsum networks. Furthermore, new reaction products in the form of white lumps were observed.

Figure 4.35 FESEM image of untreated Pink Soil

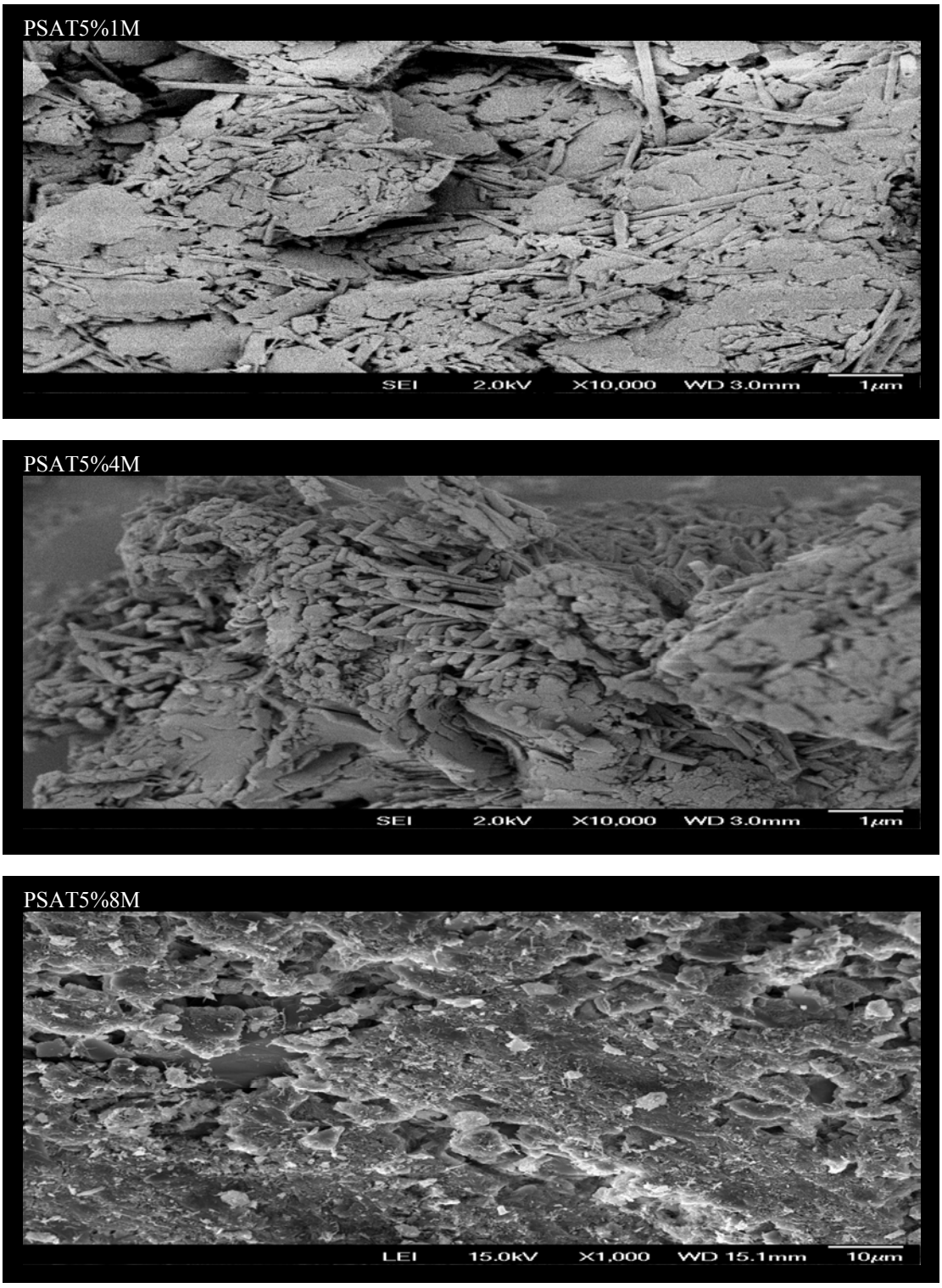


Figure 4.36 FESEM images of 5% phosphoric acid treated Pink Soil after 1month, 4months, and 8months curing time

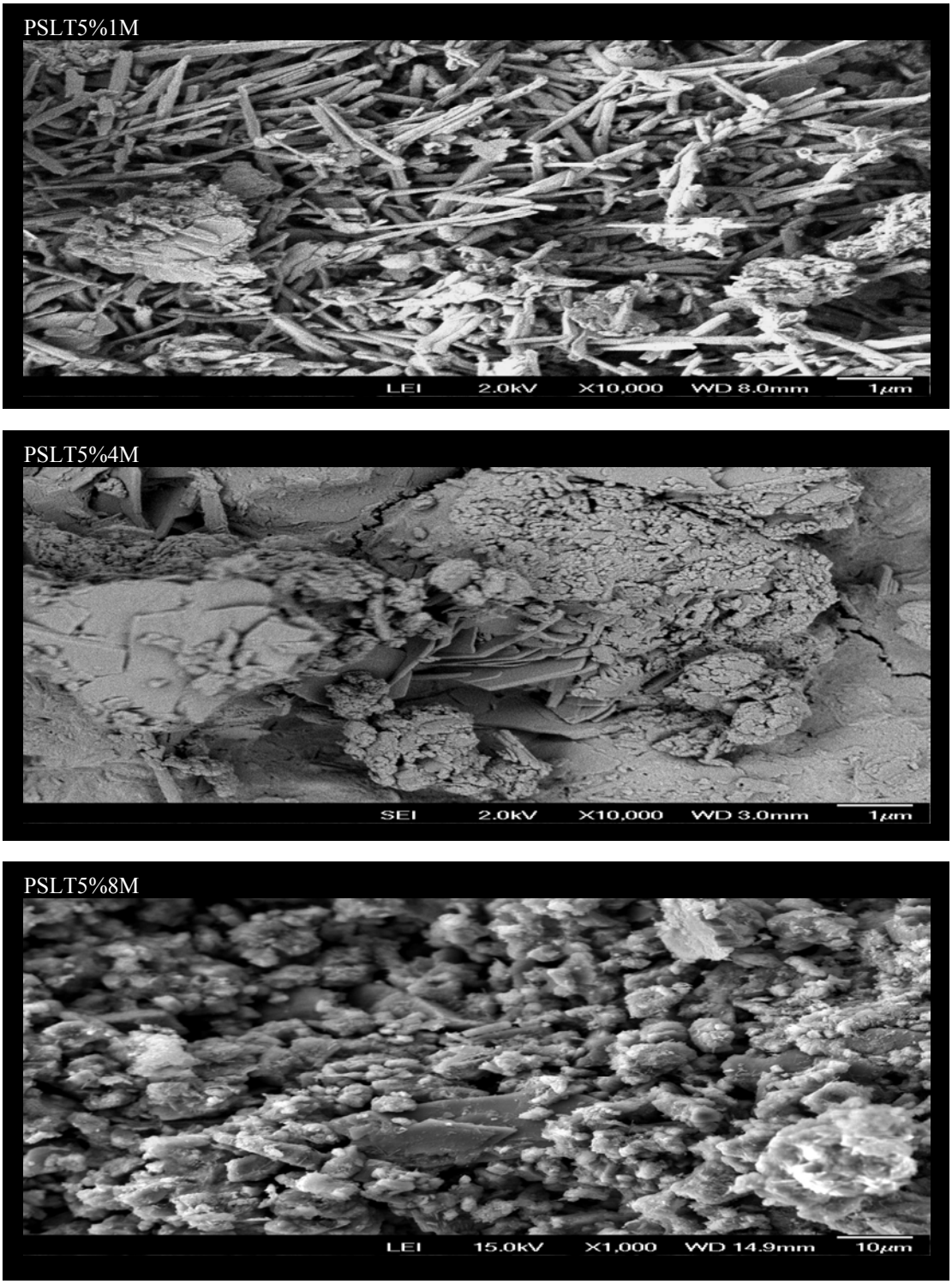


Figure 4.37 FESEM images of 5% lime treated Pink Soil after 1month, 4months, and 8months curing time

4.3.3 Molecular Characterization

4.3.3.1 FTIR Results

In this research, infrared spectroscopy was used to study the effects of stabilizers on the molecular structure of treated samples.

FTIR spectra of natural and chemically treated Bentonite soil in the middle-infrared region (400–4000 cm^{-1}) are presented in Figure 4.38. The KBr curve of untreated Green Bentonite was characteristic of montmorillonite mineral with a single sharp band at 3632 cm^{-1} followed by a broad band at 3446 cm^{-1} for OH stretching of structural hydroxyl groups and water, respectively (Madejova and Komadel, 2001). In the lower frequency region, montmorillonite also had a strong band at 1050 cm^{-1} for Si–O stretching (in-plane) vibration of layered silicates. The absorption peak in the 1640 cm^{-1} region was attributed to the OH deformation mode of water. IR peaks at 913 cm^{-1} and 885 cm^{-1} were attributed to AlAlOH and AlFeOH, respectively. The 466 cm^{-1} band was a Si-O-Si deformation, and the band at 524 cm^{-1} corresponded to the deformation mode of Al-O-Si group. The 620 cm^{-1} band was a coupled Al-O and Si-O (out-of-plane) bond. There were also some quartz present as indicated by the bands at 778 cm^{-1} and 791 cm^{-1} (Marel and Beutelspacher, 1976).

Assessment of the FTIR spectrums in acid and lime treated samples also indicated few noticeable changes. First of all, there were a slight decrease in the intensity of AlAlOH and AlFeOH bonds and a distortion at 620 cm^{-1} absorption band with curing time. These changes were probably caused by the action of stabilizers on the clay structure. In addition, new peaks at 2920 cm^{-1} and 1420 cm^{-1} with respect to 8 months cured phosphoric acid and lime treated samples were evident. These absorption bands were tentatively assigned to the P–OH bond of phosphoric acid and Ca–OH bond of lime present in the soil-stabilizer matrix (Nacamoto, 1970).

It should be noted that for comparison reasons, by using a FTIR analysis program, the absorption bands were standardized to the largest intensity present in the pattern by applying a value of 1 to this peak, hence, the other peaks were a fraction of this peak.

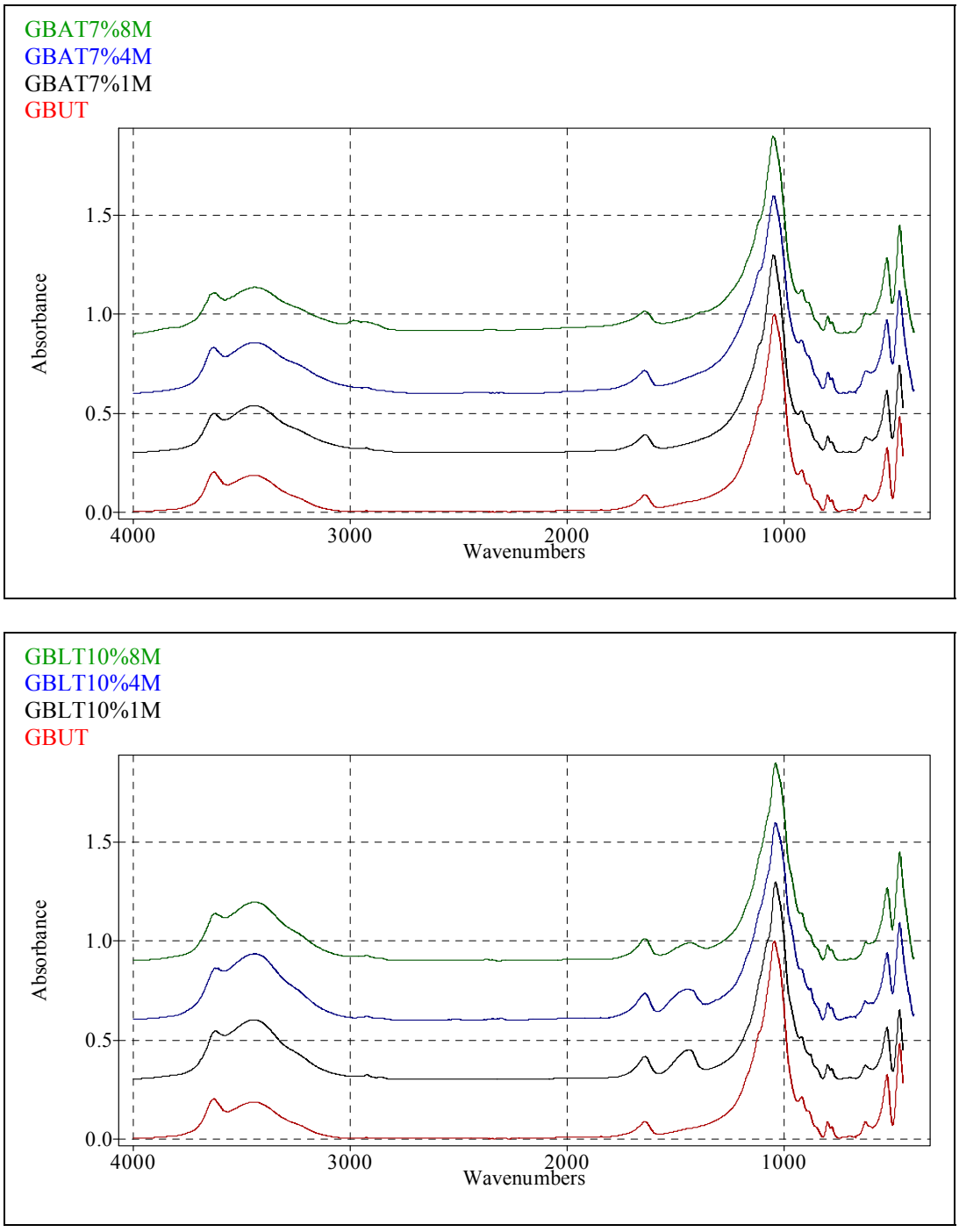


Figure 4.38 FTIR spectrums of natural, phosphoric acid and lime treated Green Bentonite at different time intervals

The common features of FTIR spectra for natural, phosphoric acid and lime treated Laterite Clay were as described (Figure 4.39). That is, the bands at 1105 cm^{-1} and 1032 cm^{-1} corresponded to the perpendicular and in-plane Si–O stretchings. Peaks at 3620 and 3696 cm^{-1} were attributed to the OH stretching vibrations of inner and inner-surface hydroxyl groups, respectively (Madejova and Komadel, 2001). The latter band is characteristic of a kaolinite mineral, while the former is commonly found in many different phyllosilicate minerals. The band at 913 cm^{-1} suggested the presence of hematite (Gadsen, 1975). There was also some quartz present as indicated by the band at 796 cm^{-1}. Most of the other bands such as the Si–O vibrations observed at 698 cm^{-1}, 540 cm^{-1}, 470 cm^{-1}, and 430 cm^{-1} confirmed the presence of kaolinite mineral. The remaining bands were assigned to water vibrations. Band at 3446 cm^{-1} was a stretching vibration, whereas the 1638 cm^{-1} band was a H–O–H bending band of water with an overtone occurring at 3378 cm^{-1}.

As can be seen from the FTIR spectrums of cured samples, the chemical treatment did not cause any major changes in the molecular structure of soil particles. However, in the lime stabilized soil, a new absorption band (1385 cm^{-1}) with a weak intensity attributed to the Ca–OH bond of lime was evident.

The FTIR spectra of natural and chemically treated White Kaolin soil are shown in Figure 4.40. As can be seen, kaolinite was characterized by two strong bands at 3696 and 3620 cm^{-1}. These bands were attributed to the octahedral OH stretching vibrations. In the finger print region, kaolinite revealed sharp bands at 1105 cm^{-1}, 1033 cm^{-1}, and 1008 cm^{-1} attributed to the Si-O stretching and at 937 cm^{-1} and 914 cm^{-1} corresponding to the OH deformation of hydroxyl groups. Most of the other bands such as the Si–O vibrations observed at 791 cm^{-1}, 698 cm^{-1}, 540 cm^{-1}, 470 cm^{-1}, and 430 cm^{-1} also confirmed the presence of kaolinite mineral.

Similar to Laterite Clay samples, apparently there were no significant changes in the FTIR spectra of acid and lime treated samples. Nevertheless, it seemed to be a slight decrease in the intensity of absorption band at 1105 cm^{-1}. Also, in lime treated samples, a new peak at 1385 cm^{-1} was observed.

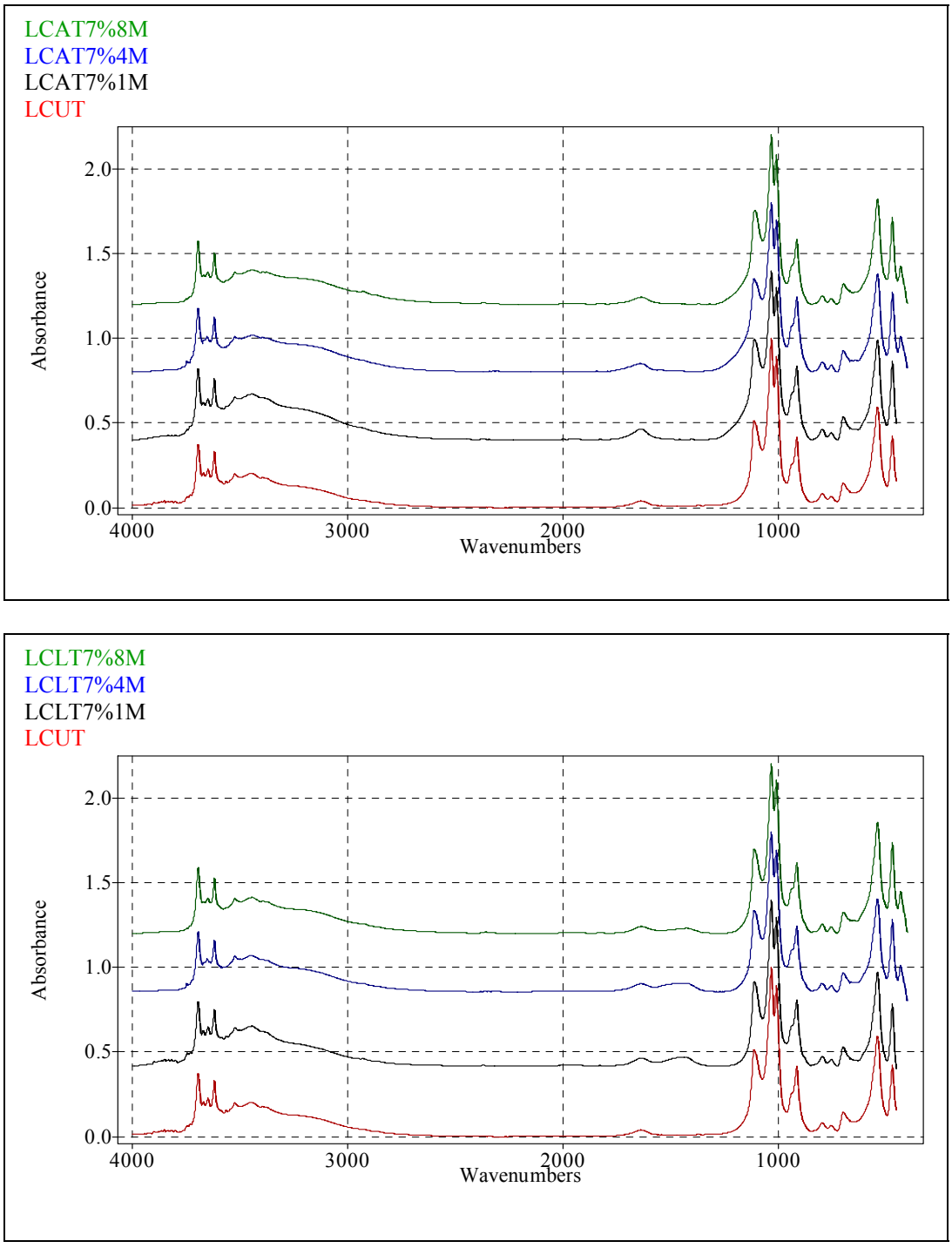


Figure 4.39 FTIR spectrums of natural, phosphoric acid and lime treated Laterite Clay at different time intervals

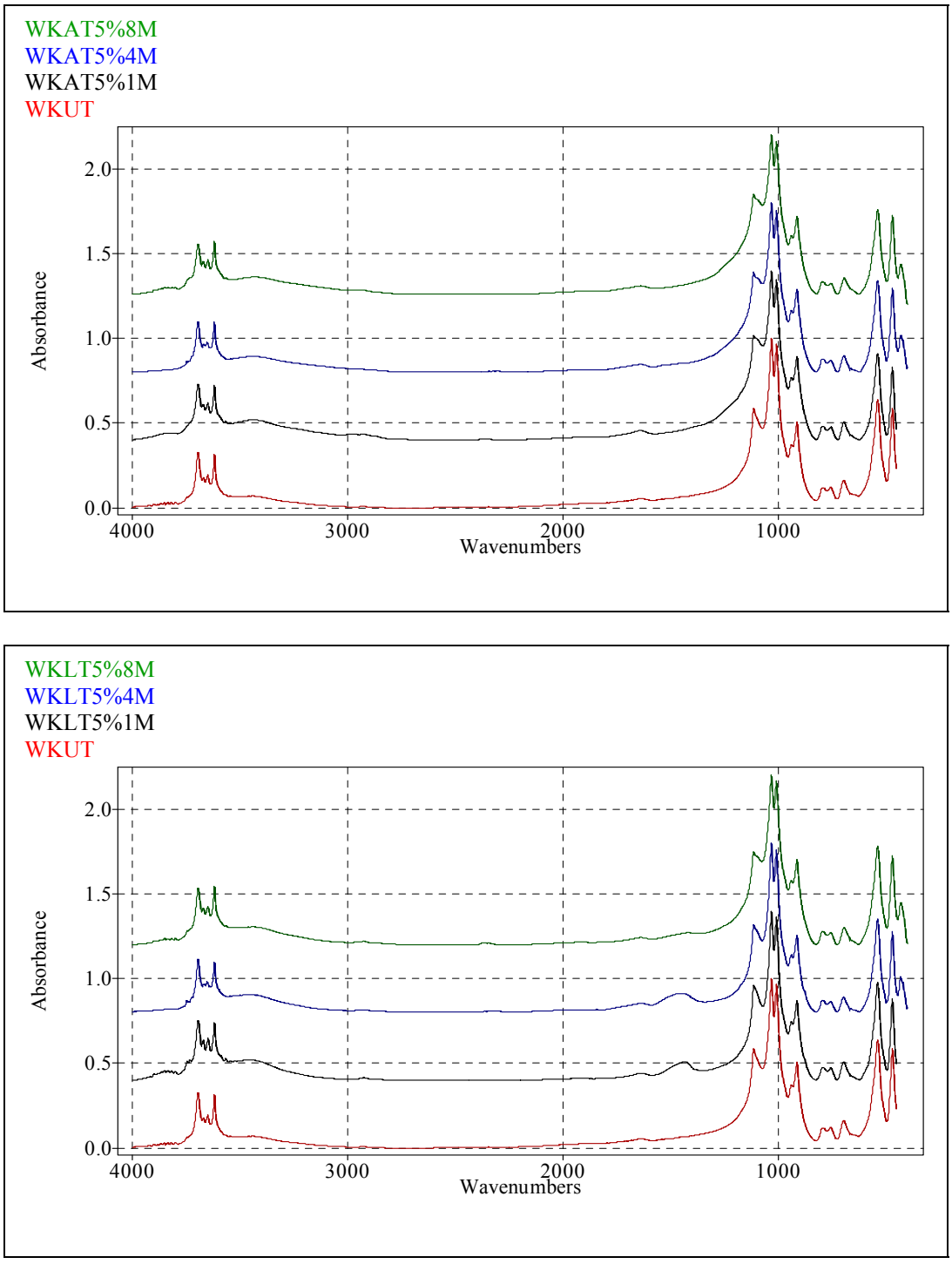


Figure 4.40 FTIR spectrums of natural, phosphoric acid and lime treated White Kaolin at different time intervals

FTIR spectroscopy was conducted on untreated, phosphoric acid and lime treated Pink Soil after 1, 4, and 8 months of curing time (Figure 4.41). The functional groups identified from the peaks in the FTIR spectra are presented in Table 4.7.

Table 4.7 : Interpretation of peaks in the FTIR spectra of Pink Soil

Wavelength (cm^{-1})	**Functional Group**
430	Si-O deformation
470	Si-O-Si deformation
540	Al-O-Si deformation
695	Si-O perpendicular
796	Si-O
914	OH deformation of inner hydroxyl groups
937	OH deformation of inner-surface hydroxyl group
1008	in-plane Si-O stretching
1033	in-plane Si-O stretching
1115	Si-O stretching (longitudinal mode)
1385	Ca-OH
3620	OH stretching of inner hydroxyl groups
3651	OH stretching of inner-surface hydroxyl groups (Anti-phase vibration)
3672	OH stretching of inner-surface hydroxyl groups (Anti-phase vibration)
3696	OH stretching of inner-surface hydroxyl groups (In-phase vibration)

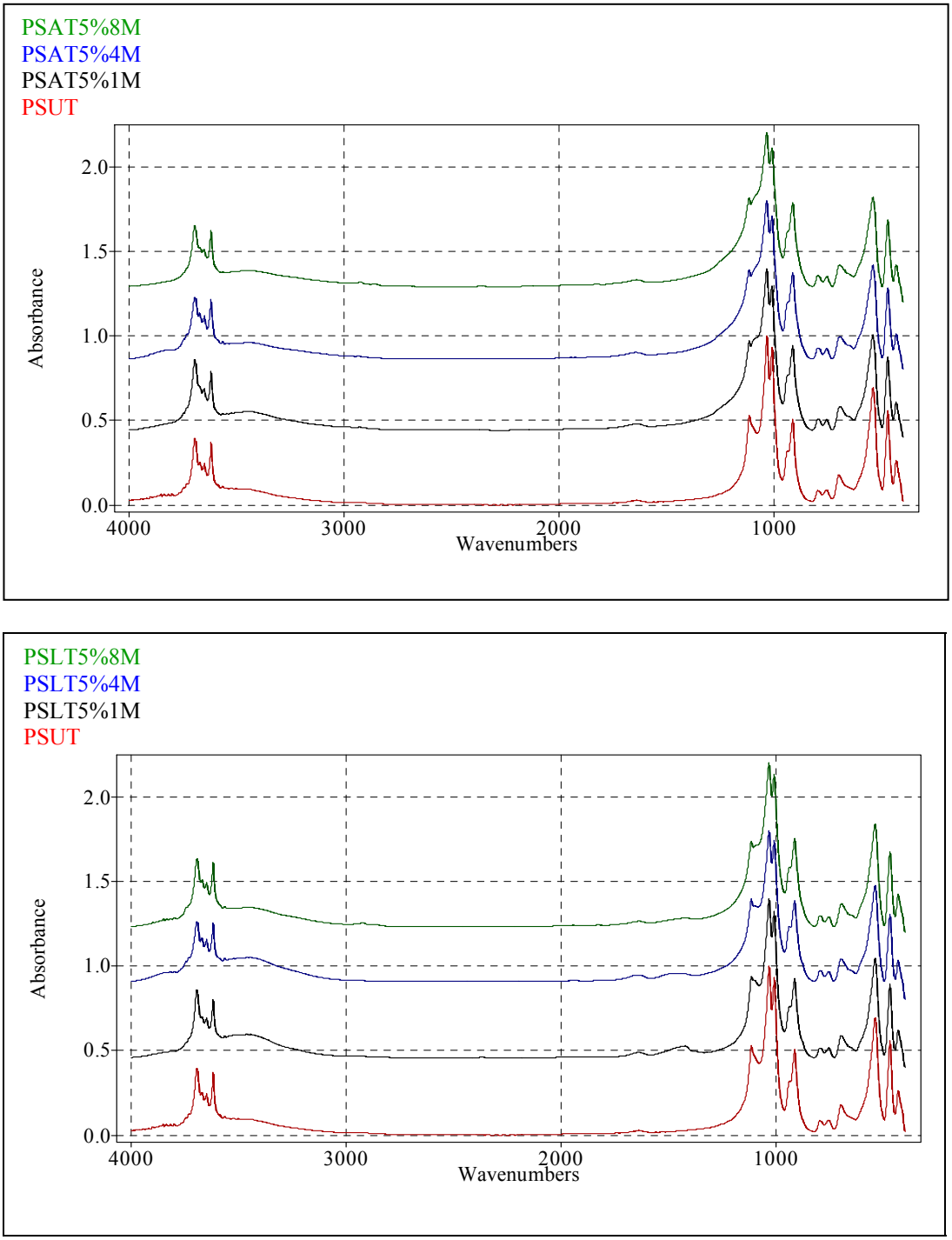


Figure 4.41 FTIR spectrums of natural, phosphoric acid and lime treated Pink Soil at different time intervals

4.3.3.2 NMR Results

Solid-state ^{29}Si and ^{27}Al NMR spectroscopy has provided useful information regarding the Si and Al distribution in the tetrahedral and octahedral sites of natural soil minerals (Barron *et al*., 1985). In this research, ^{27}Al and ^{29}Si MAS NMR spectroscopy were performed on untreated and 8 months cured Green Bentonite and Laterite Clay mix designs in order to further elucidate the mechanisms observed in the stabilization process.

As can be seen in Figure 4.42, the spectrum of untreated Green Bentonite showed a relatively sharp symmetric band at approximately 57ppm corresponding to the tetrahedrally coordinated Al, and a broad peak at 2ppm arising from octahedral Al (Okada *et al*., 2006). After 8 months of curing, the ^{27}Al NMR spectra revealed the same tetrahedral peak to the original peak for the stabilized samples. Nevertheless, there was a slight difference in the value and the intensity of octahedral Al peaks with the former shifting to -2ppm and -1ppm for acid and lime treated samples, respectively. The results suggested a similar local structure to the original structure of the natural soil.

Figure 4.43 shows the ^{29}Si MAS NMR spectrums of the untreated and lime treated Bentonite sample after 8 months of curing. The spectrum of the natural soil revealed a Q_3 peak at -94ppm corresponding to the tetrahedral layers of clay silica. One sharp peak at -108.5ppm representing quartz in Q_4 arrangements was also observed.

As can be seen, the addition of lime does not seem to bring any major alterations in the structure of the tri-dimensional (Q_4) quartz particles. Nevertheless, some changes in the bi-dimensional (Q_3) clay minerals were observed. In addition, the presence of a new peak at about -84ppm corresponding to the Q_2 structure was apparent (Cong and Kirkpatrick, 1996). The latter was probably caused by the weathering action of lime on the crystalline clay structure and its subsequent conversion from Q_3 to Q_2.

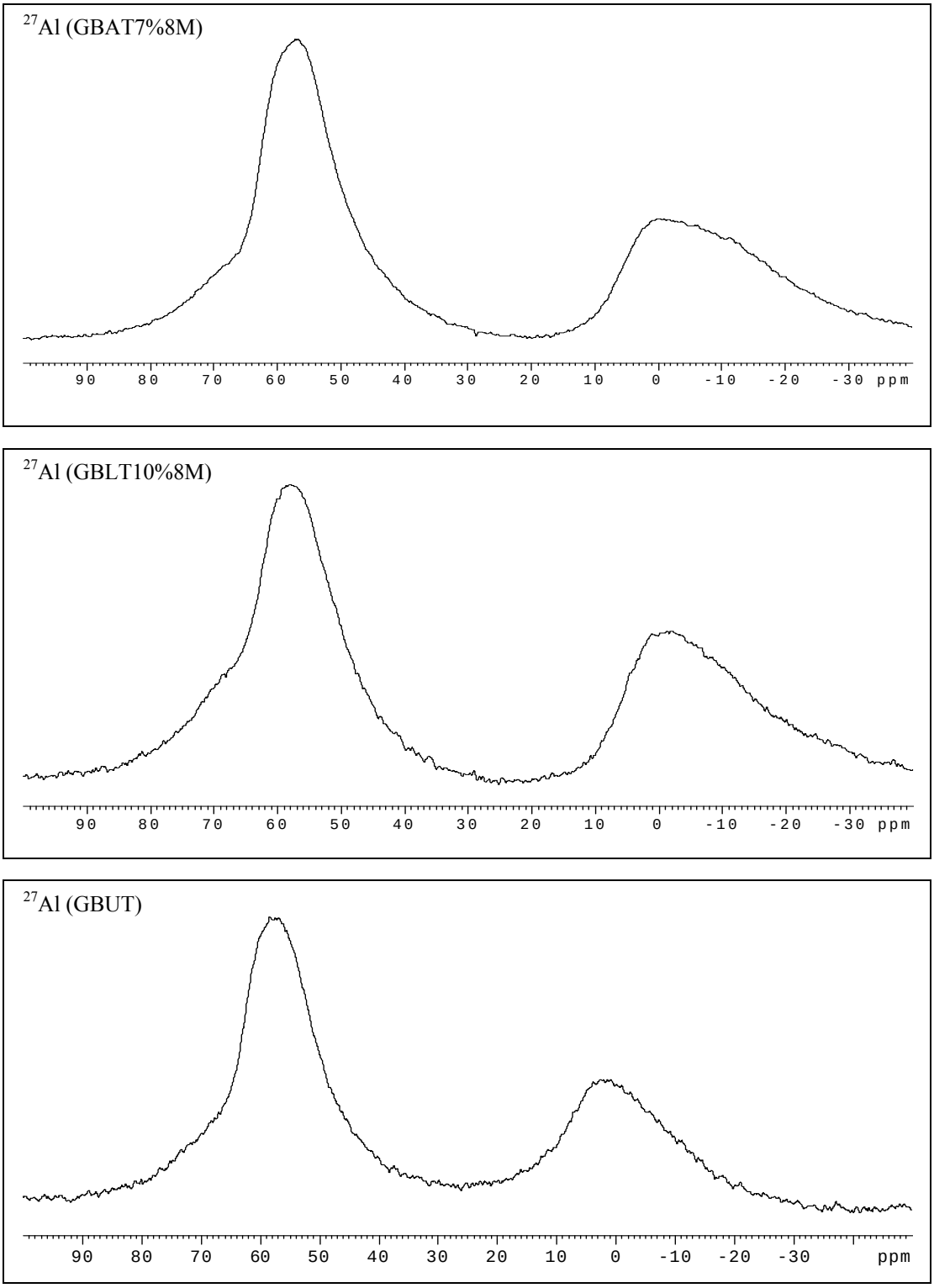


Figure 4.42 ^{27}Al MAS NMR spectra of natural, lime and phosphoric acid treated Green Bentonite after 8 months of curing

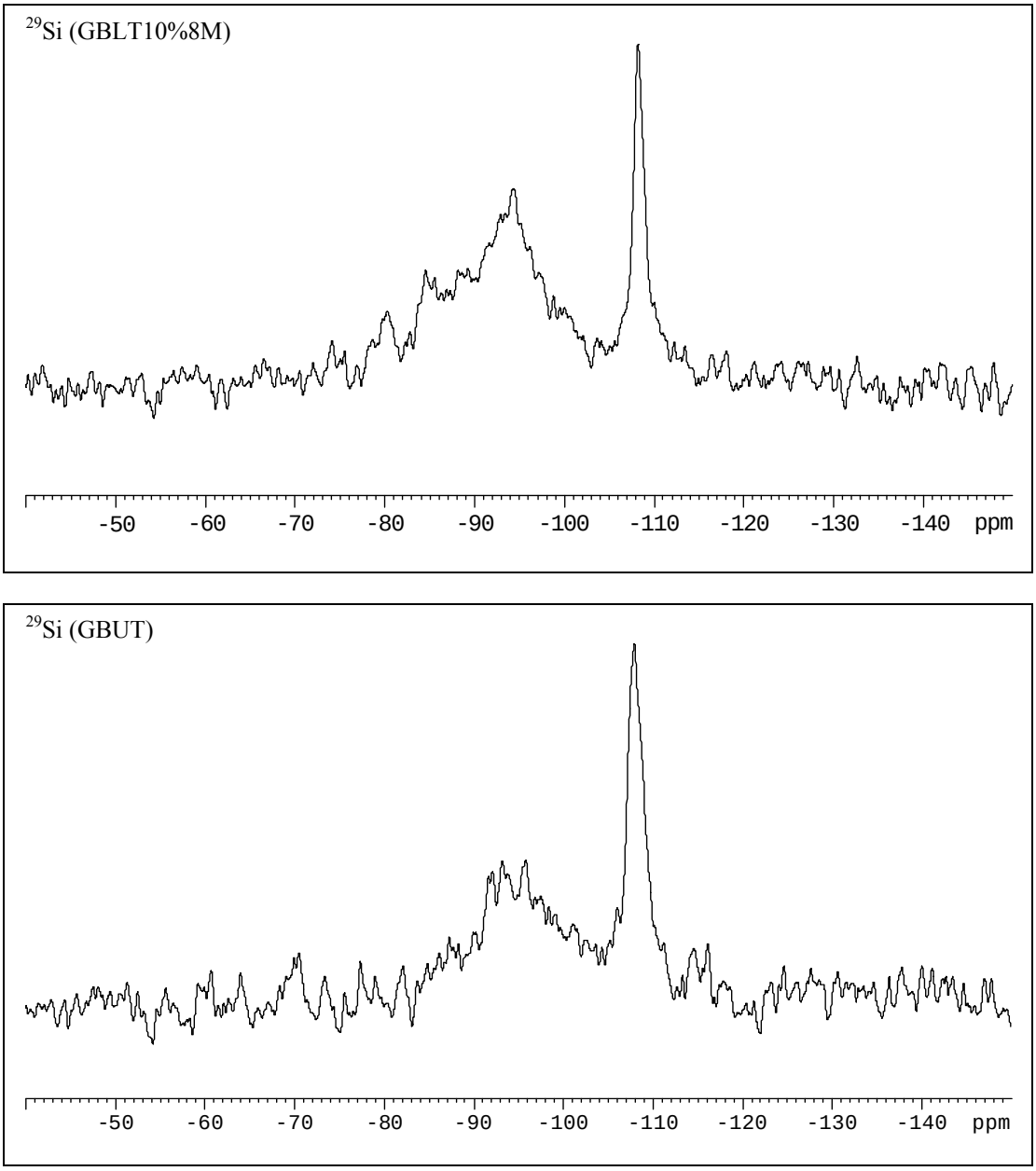


Figure 4.43 ^{29}Si MAS NMR spectra of natural and lime treated Green Bentonite after 8 months of curing

As can be seen, in the ^{27}Al NMR spectrum of the natural lateritic soil (Figure 4.44), a broad peak at 70ppm corresponding to the tetrahedral Al, and a relatively sharper peak at approximately 0ppm arising from the octahedral Al were observed. The intensity of octahedral peak supported the presence of kaolinite mineral with 1:1 silica: alumina structure in the soil environment.

After 8 months of curing, the spectrum of phosphoric acid treated samples revealed slightly different local structure to that of the natural soil. That is a tetrahedrally coordinated Al band at approximately 73.5ppm and a octahedrally coordinated Al band at 5.5ppm. However, for lime treatment the molecular structure was essentially similar to that of the natural soil.

As was mentioned in the literature review, the ^{29}Si MAS spectroscopy provides valuable information regarding the chemical environment of the silicon atoms, distinguishing between the microcrystalline and the amorphous phases. In addition, the different organizations of the tetrahedral in mono-, bi-, or tri-dimensional structures can be detected with the MAS ^{29}Si spectroscopy, as they give rise to different signals resonating in well-defined chemical shift intervals.

The ^{29}Si NMR spectra of untreated and lime treated Laterite Clay is shown in Figure 4.45. As seen, the spectrum of the natural soil revealed a major peak at −92ppm with smaller shoulders at −88 and -95ppm. These peaks were attributed to the bi-dimensional (Q_3) clay structure. Although, after 8 months of curing, some marginal variation in the size and intensity of main peak located at −92ppm was evident, however, no new peaks or chemical shifts in the structure of lime treated clay particles were observed.

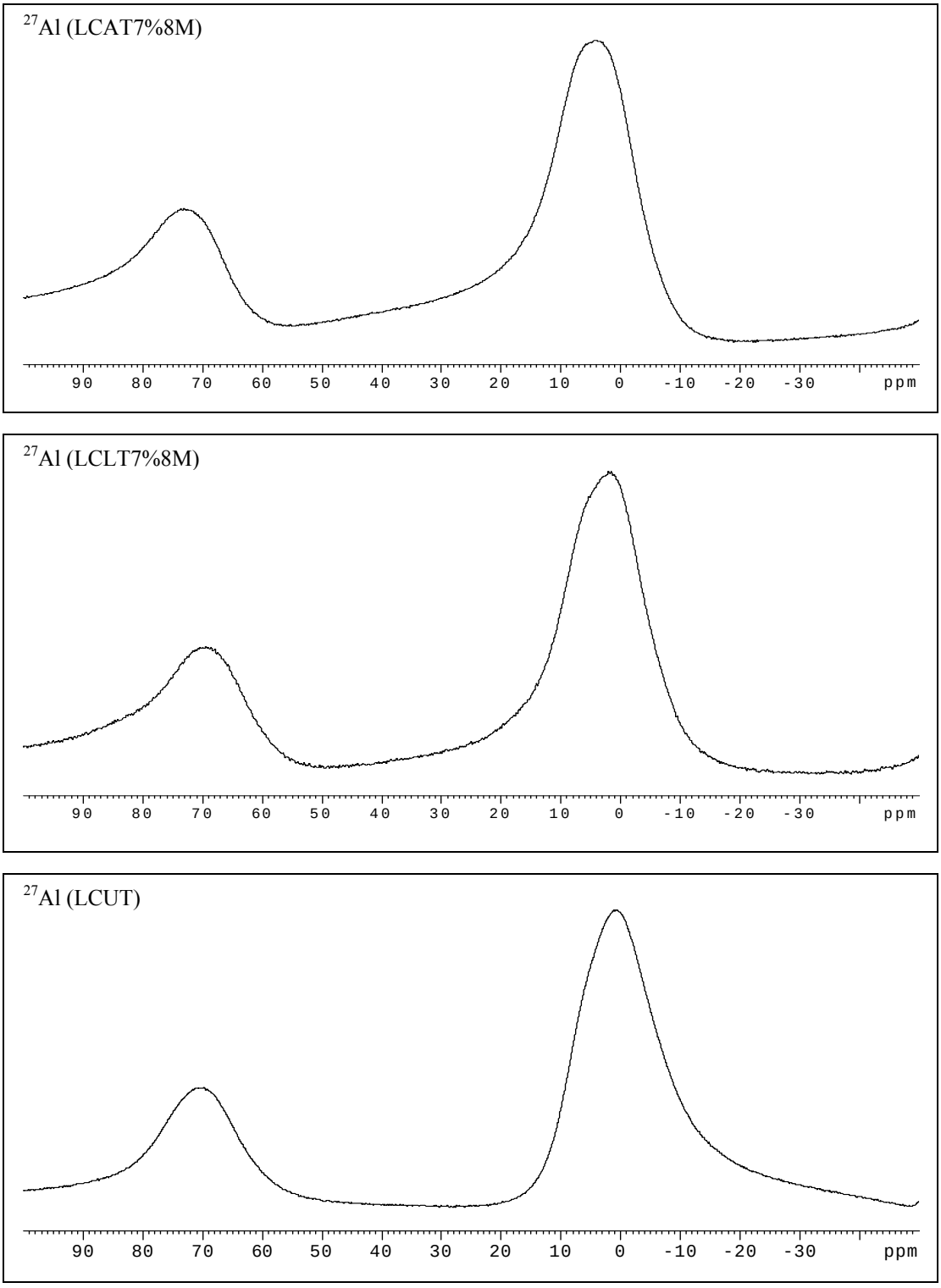


Figure 4.44 ^{27}Al MAS NMR spectra of natural, lime and phosphoric acid treated Laterite Clay after 8 months of curing

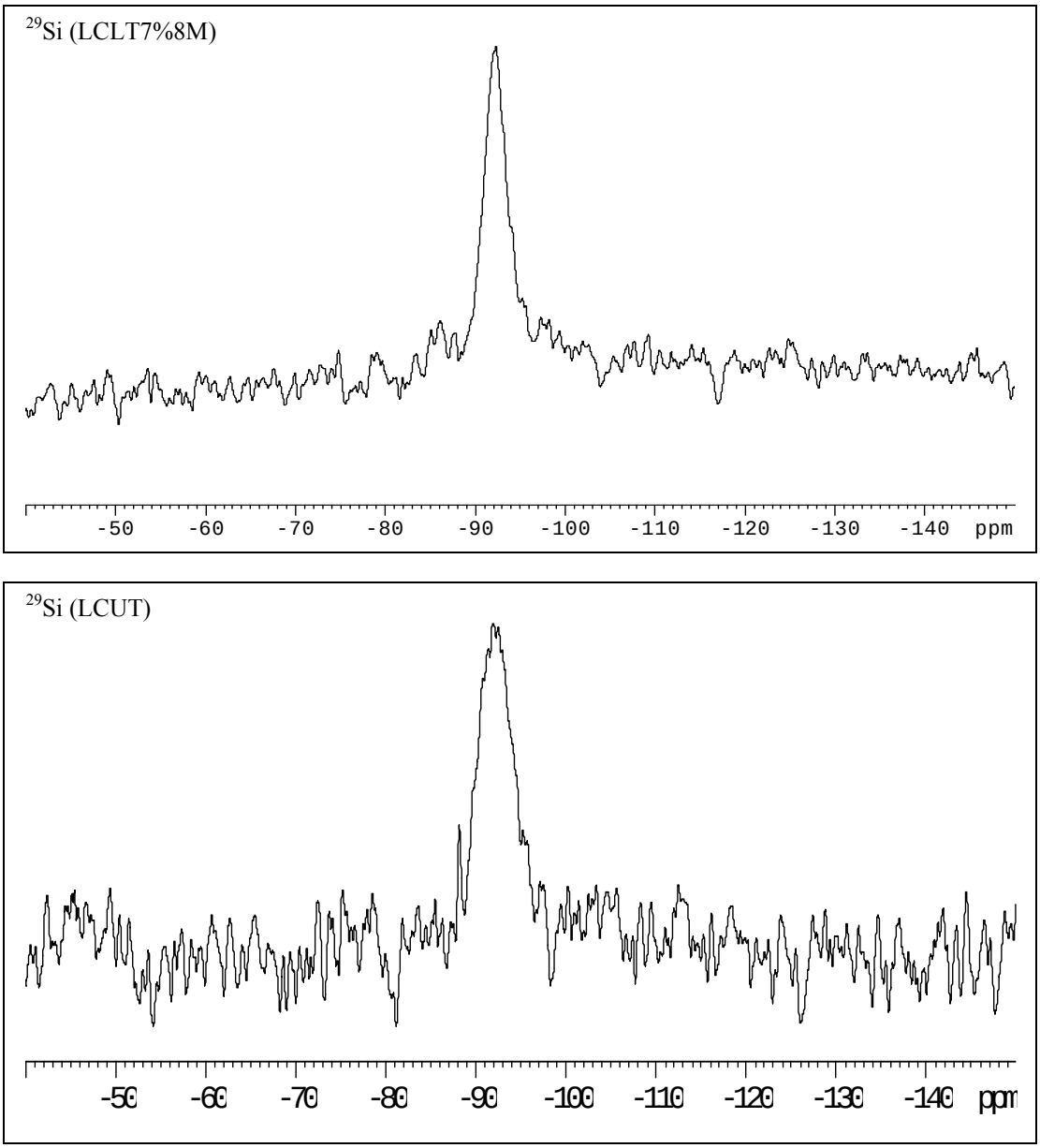


Figure 4.45 ^{29}Si MAS NMR spectra of natural and lime treated Laterite Clay after 8 months of curing

4.4 Chemical Analysis of Cured Samples

4.4.1 pH Results

In this thesis, the pH analysis was performed to determine the variations in H_3O^+ ion concentration of pore water. In Figure 4.46, the pH values for Green Bentonite design mixes are demonstrated. As can be seen, with respect to lime and phosphoric acid treatment, a reduction and a rise in the pH of soil solution was apparent. Moreover, the acid treated samples in comparison to lime mix designs, revealed greater changes in the first 4 months curing period. This was expected due to the highly alkaline nature of the natural soil (pH=9.03). It was also clear that as the amount of stabilizer (10% lime & 7% phosphoric acid) and curing time increased the variation in pH value were more significant implying that the stabilizer content was predominantly controlling the pore water chemistry.

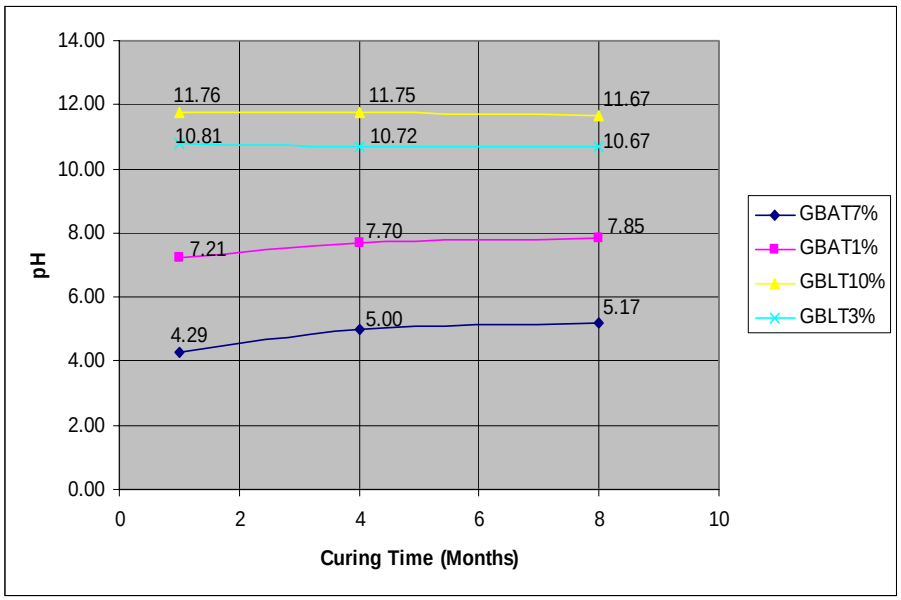


Figure 4.46 Variation of pH for Green Bentonite mix designs

Figure 4.47 shows the changes in pH value of lime and phosphoric acid treated Laterite Clay samples with curing time. As seen, in comparison to the Bentonite soil, the acid treatment reduced the pH of the solution to a greater intensity. The latter was due to the acidic nature of the untreated soil (pH=4.86). Whereas, the pH value for lime treated samples showed a similar rise.

Figure 4.48 shows the time-dependent pH changes for various White Kaolin design mixes. As evident, the addition of stabilizers caused wider changes in the pH value of chemically treated White Kaolin samples in comparison to the other three soil types. The importance of a broader pH variation was due to the presence of pH-dependent alumina and hydroxyl groups on the surface of kaolinite particles and the fact that at a high or low pH the clay edges acquired negative or positive charged sites attracting cations and anions, respectively.

Figure 4.49 highlighted a similar pH pattern for the Pink Soil design mixes. The trends for hydrogen ion concentration (pH) appeared relatively clear. The most apparent difference was the fact that as the percentage of lime increased from 1% to 5% at 1 month curing period, the gain in pH value was much lower than the White Kaolin samples. This was attributed to the reduction of lime ions in the pore water.

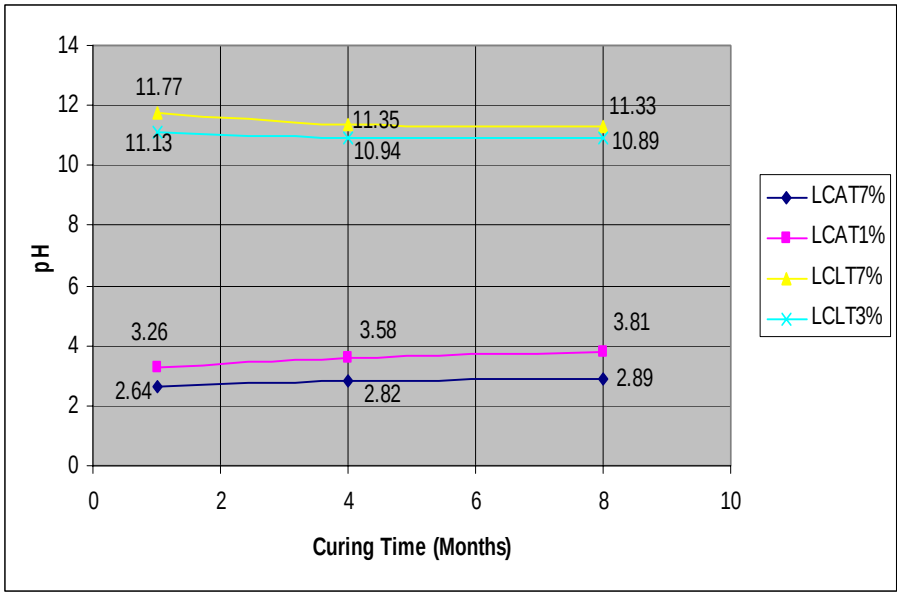


Figure 4.47 Variation of pH for Laterite Clay mix designs

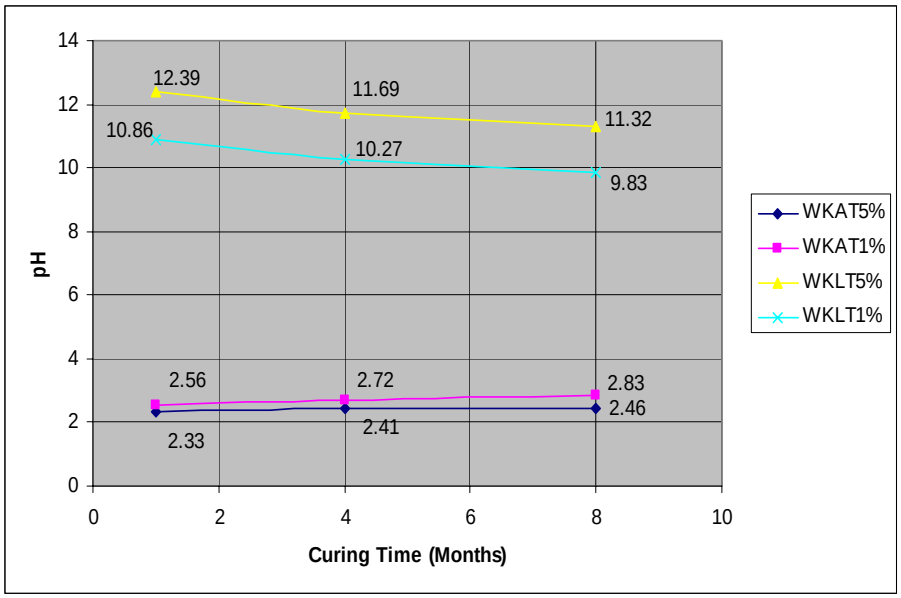


Figure 4.48 Variation of pH for White Kaolin mix designs

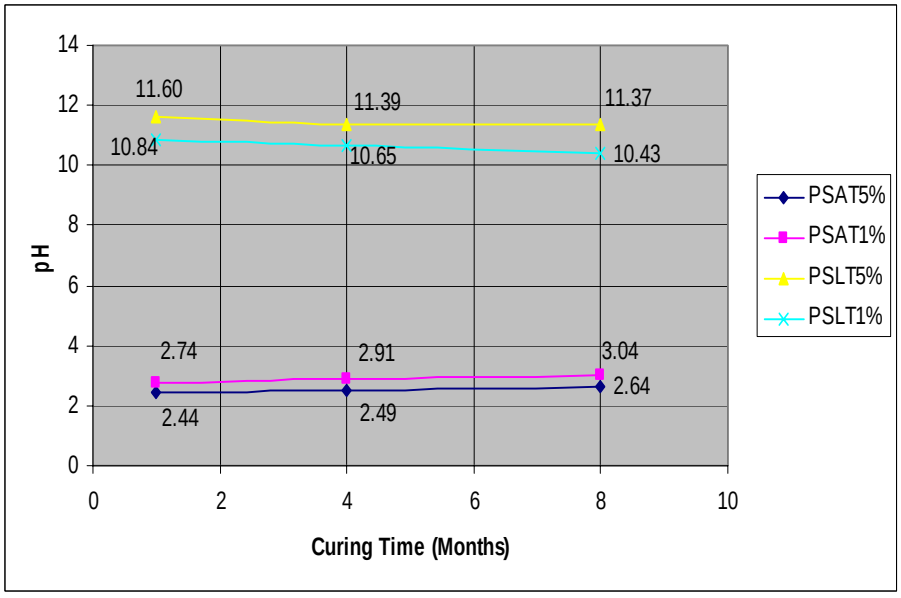


Figure 4.49 Variation of pH for Pink Soil mix designs

4.4.2 CEC Results

The cation exchange capacity caused by permanent charges (CEC_p) was measured for untreated and treated Bentonite samples with 7% and 10% acid and lime content, respectively. These mix designs were chosen since they showed the highest degree of improvement at various time intervals. It was evident from the graphs presented in Figure 4.50 that at the early stages of curing, in contrast to lime stabilized soils, acid treatment caused a significant decline in the CEC_p value of the material. This could be explained by the decrease in the pH value of the medium and also the subsequent protonation of the clay minerals which limited the accessibility to the exchange sites. Furthermore, in lime stabilized soil the increase in OH^- ion concentration of pore water and moreover the dissolution of clay silica with higher valence in comparison to the soluble alumina in acid treated samples contributed to a relatively higher CEC_p values (Ma and Eggleton, 1999). Nevertheless, at 4 months curing period, a drop in the CEC_p value of lime treated samples was observed. This was probably caused by a reduction in the OH^- ion concentration of pore water which resulted in development of less negative charges on the surface of clay particles (Grim, 1968). On the other hand, with further curing, the increase in number of broken bonds around the edges of particles in the soil-stabilizer matrix and moreover the formation of silicate and aluminate hydrate compounds that acquired negative charges contributed to the CEC_p of the material, thus increasing the CEC_p value at 8 months curing period.

CEC_p for lime and phosphoric acid treated lateritic soil with 7% stabilizer content are shown in Figure 4.51. As can be seen, the lime treatment caused a significant increase in the CEC_p value after 1 month of curing. This was probably due to the development of negative charges at the edges and surface hydroxyl groups of soil particles, as indicated by much higher concentration of soluble aluminum in the pore water of lime stabilized samples (Ma and Eggleton, 1999). At 4 months curing, a reduction in the CEC_p values of lime and acid treated mixes were observed. The limited accessibility to the exchange sites could have been the main reason responsible for this type of behavior. On the other hand, with increasing curing time from 4 to 8 months, the CEC_p value of chemically treated samples increased. This

was probably due to a rise in the number of broken bonds around the edges of particles in the soil-stabilizer matrix.

The time-dependent changes in the CEC_p value of phosphoric acid and lime stabilized White Kaolin soil is shown in Figure 4.52. The results emphasized on the fact that the charge developments on the surface of exposed hydroxyl groups had a noticeable impact on the overall CEC_p value of kaolinite mineral. For instance, in lime treated samples with higher pH values, due to an increase in the number of surface hydroxyls which lost H^+ ion and became negatively charged, an increase in the CEC_p value was observed (Ma and Eggleton, 1999). On the other hand, the protonation of soil structure and also the amphoteric nature of clay alumina which ionizes positively in a low pH environment gave rise to a lower CEC_p values in the acid treated samples. Furthermore, the CEC_p value of phosphoric acid mix designs did not reveal a significant change with increasing curing time.

CEC_p value for untreated and 5% lime and phosphoric acid treated Pink soil are shown in Figure 4.53. As can be seen, the lime treatment caused a sharp increase in the CEC_p value after 1 month of curing. This was probably due to an increase in the number of negatively charged surface hydroxyl groups and the formation of new reaction products. At 4 months time interval, a reduction in the CEC_p values of both design mixes was observed. However, with further curing to 8 months, no considerable changes in the CEC_p value were observed.

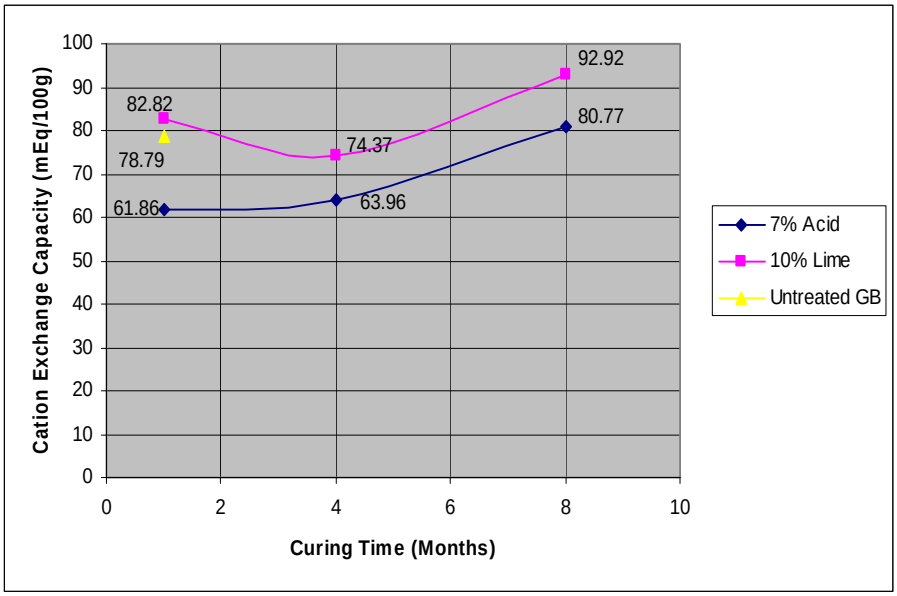


Figure 4.50 Time-dependent changes in CEC_p of Green Bentonite samples

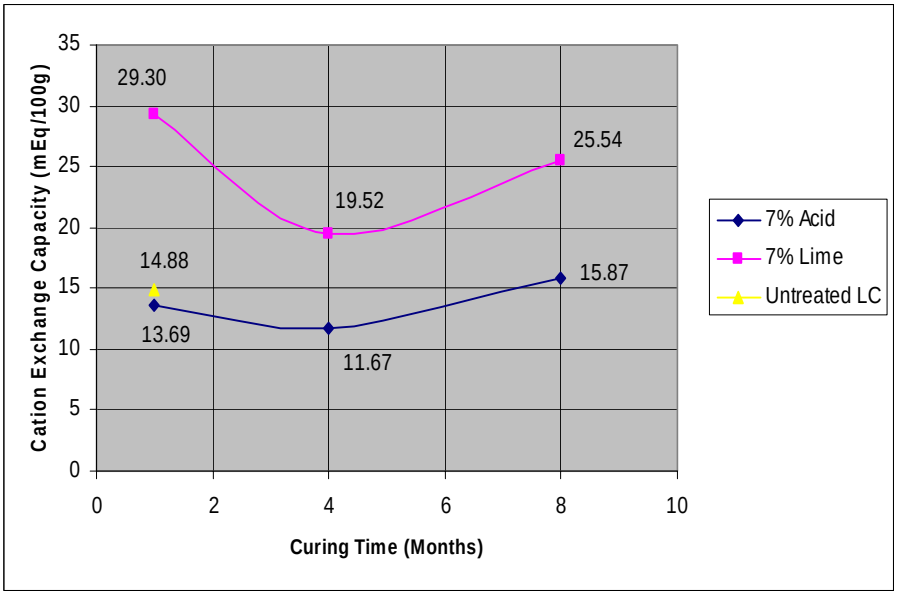


Figure 4.51 Time-dependent changes in CEC_p of Laterite Clay samples

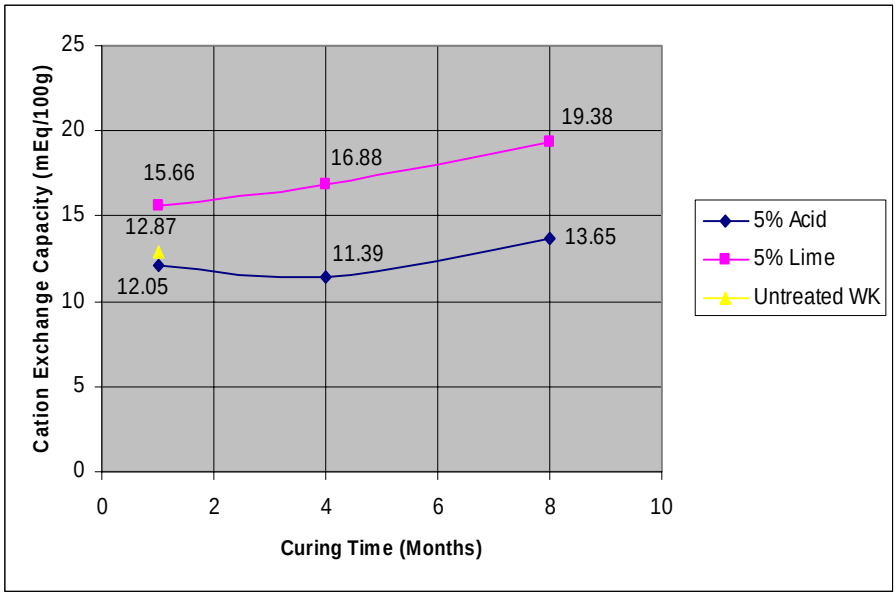


Figure 4.52 Time-dependent changes in CEC_p of White Kaolin samples

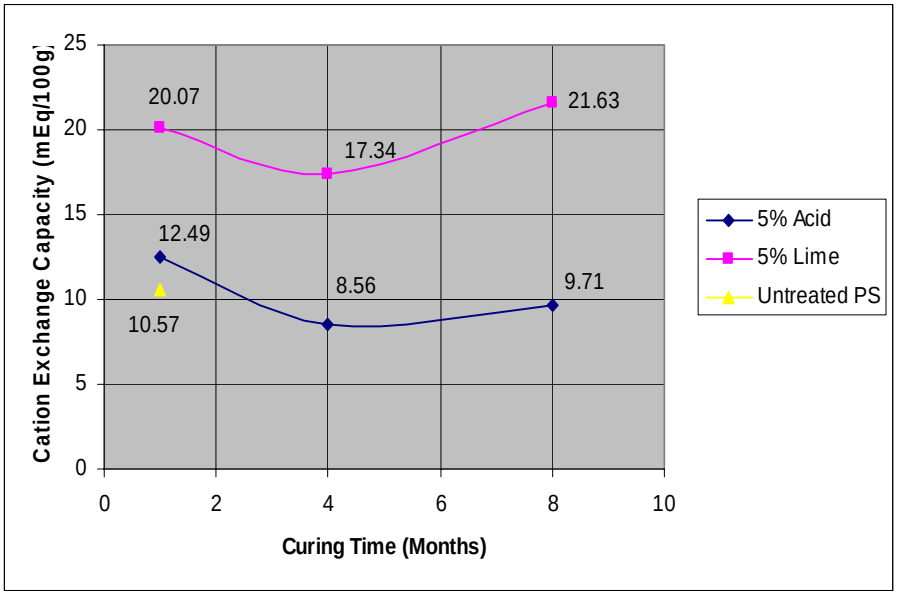


Figure 4.53 Time-dependent changes in CEC_p of Pink Soil samples

4.4.3 TGA Results

Figures 4.54 and 4.55 show the thermal gravimetric curves of phosphoric acid and lime treated Bentonite soil after 4 and 8 months of curing along with the reference untreated sample (refer to **Appendix E** for samples of data obtained from TGA analysis). As can be seen, soil dehydration covered the temperature range between 72ºC to 231ºC, with its maximum occurring at 105ºC for 4 months cured lime samples. This weight loss was due to the evaporation of the adsorbed water on the surface and inter-layer of montmorillonite minerals. Furthermore, in both of the mix designs and after 8 months of curing, a drop at around 270ºC was evident. This was tentatively caused by the evaporation of moisture encapsulated in the crystallized reaction products. Also, the loss at approximately 650ºC observed in all mix designs was due to the dehydroxylation of montmorillonite mineral (Guggenheim and van Groos, 2001).

The thermal analysis patterns of phosphoric acid and lime stabilized Lateritic soil are presented in Figures 4.56 and 4.57, respectively. As can be seen in the untreated and treated samples, considerable amounts of organic matter were present. The weight losses at temperatures around 300°C was due to this phenomenon. In addition, similar to the Bentonite soil, evaporation of adsorbed surface water was the main reason responsible for the weight losses observed in the lower temperature regions (50ºC to 104ºC). The drop at around 515ºC observed in all Laterite Clay design mixes was tentatively assigned to the dehydroxylation of kaolinite mineral (Guggenheim and van Groos, 2001).

Evaluation of the TGA results for the 8 months cured phosphoric acid and lime treated samples also revealed a marginal drop in the weight of both samples at approximately 650ºC. This best corresponded to the dehydroxylation of kaolinite mineral, although it could not be identified with certainty.

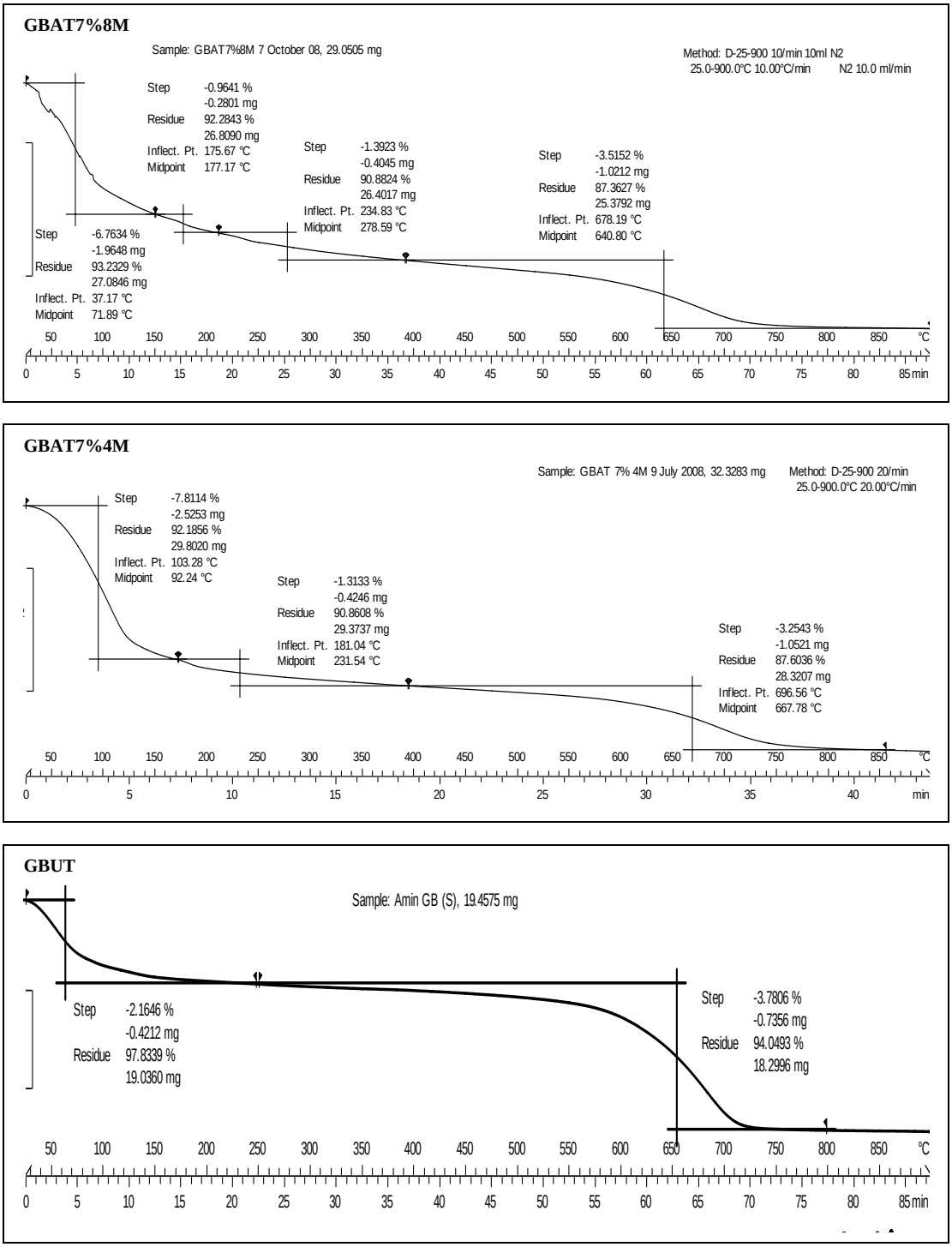
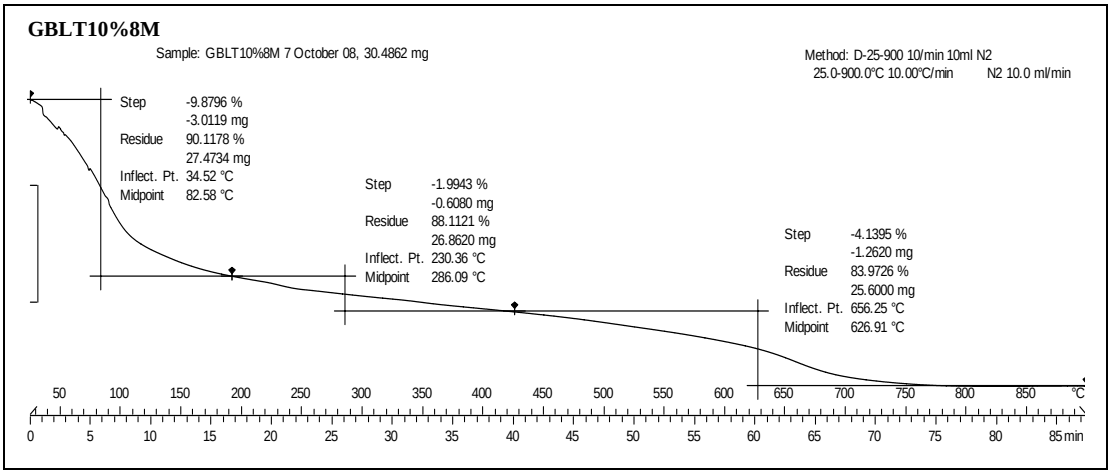
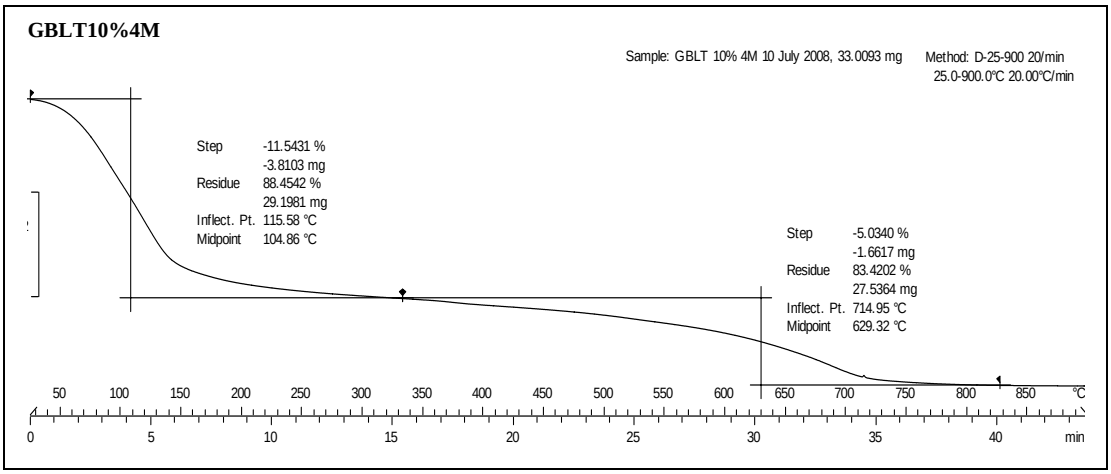


Figure 4.54 TGA spectrums of untreated and 7% phosphoric acid treated Green Bentonite





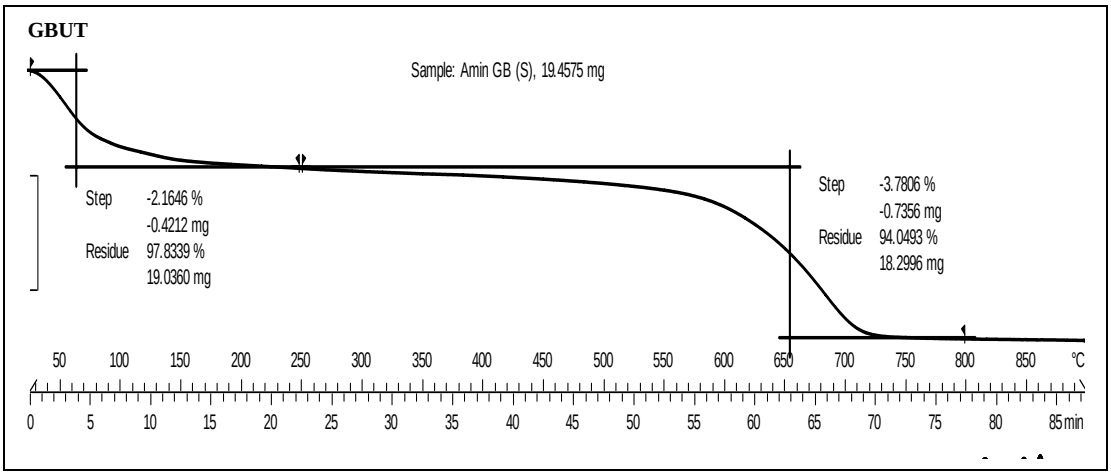


Figure 4.55 TGA spectrums of untreated and 10% lime treated Green Bentonite

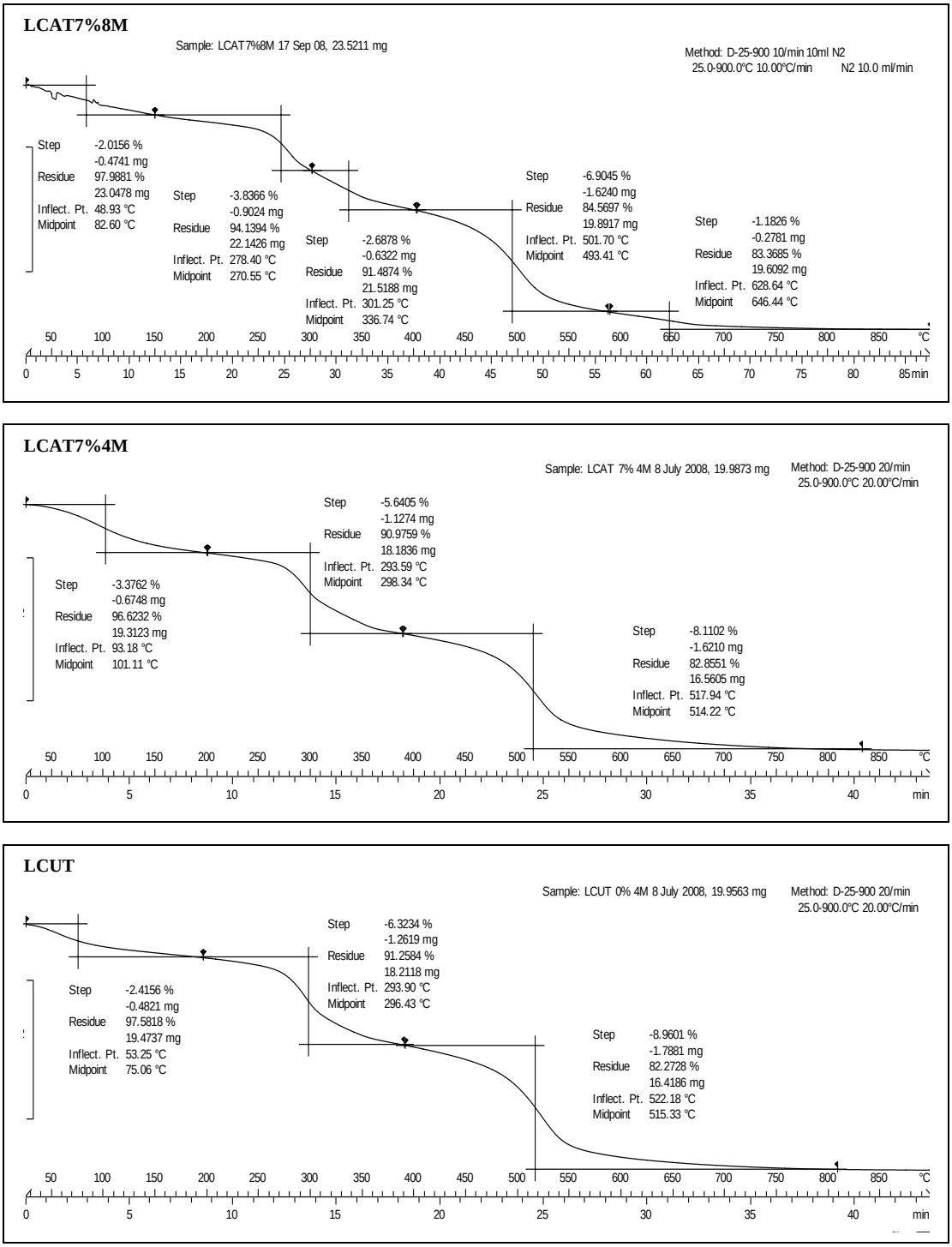


Figure 4.56 TGA spectrums of untreated and 7% phosphoric acid treated Laterite Clay

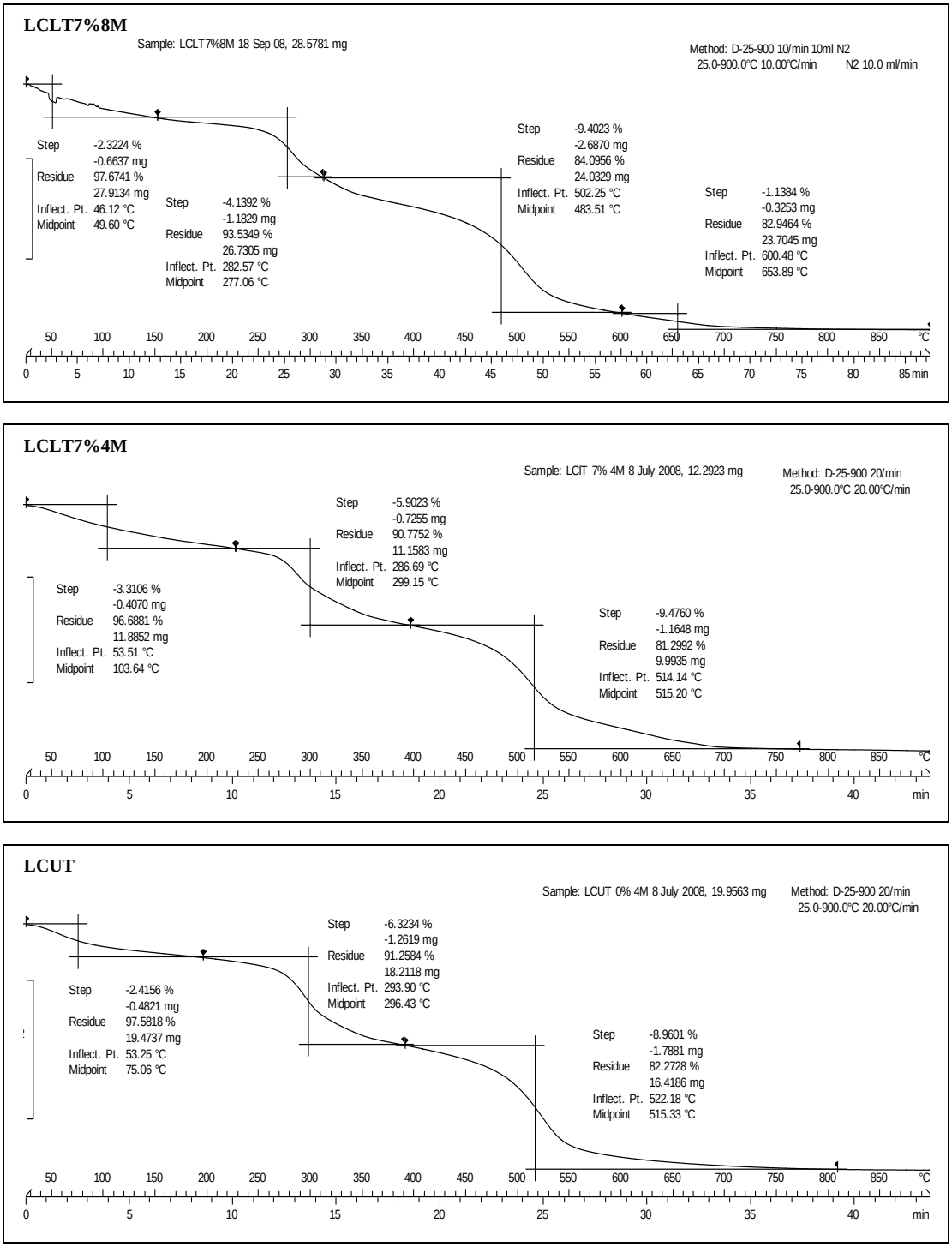


Figure 4.57 TGA spectrums of untreated and 7% lime treated Laterite Clay

In Figures 4.58 and 4.59, the thermal analysis patterns of untreated, phosphoric acid and lime treated White Kaolin samples are presented. In the natural soil, two weight losses at approximately 80ºC and 550ºC were evident. The latter was attributed to the dehydroxylation of kaolinite mineral, while the former was caused by the dehydration of soil particles. Furthermore, in both of the mix designs and after 8 months of curing, a drop at around 250ºC was observed. This was tentatively assigned to the evaporation of moisture encapsulated in the crystallized reaction products. In addition, similar to Bentonite samples, no traces of impurities affecting the results were found.

The TGA graphs of natural and chemically treated Pink Soil are presented in Figures 4.60 and 4.61. As can be seen, the presence of small amount of impurities at around 280°C was apparent. In addition, similar to the 8 months cured Laterite Clay samples, a noticeable weight loss at approximately 620ºC and 730ºC with respect to phosphoric acid and lime treatment were observed. These drops were probably due to the dehydroxylation of kaolinite mineral. Also, the evaporation of adsorbed surface water was believed to be the main reason responsible for the weight losses observed in the lower temperature regions.

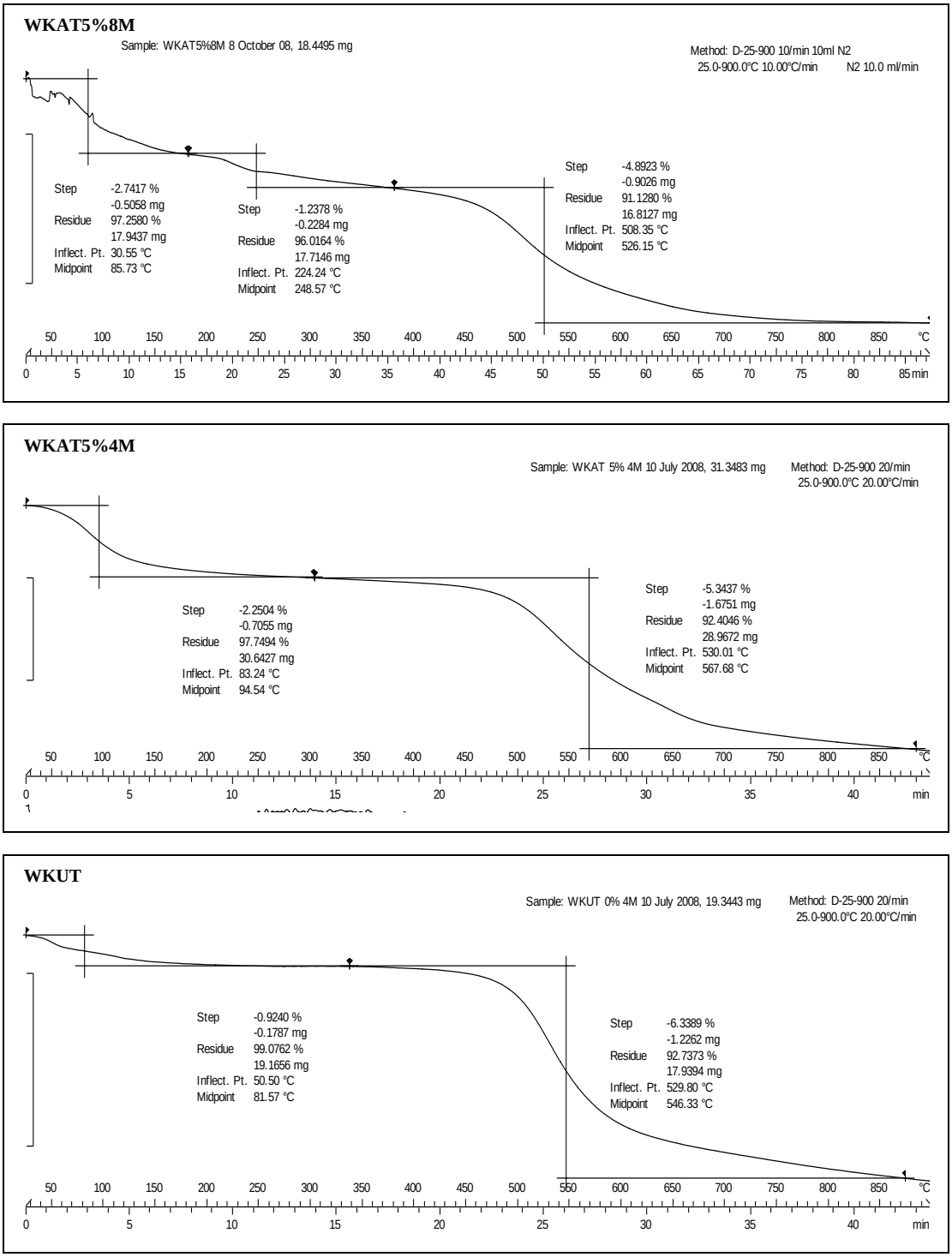


Figure 4.58 TGA spectrums of untreated and 5% phosphoric acid treated White Kaolin

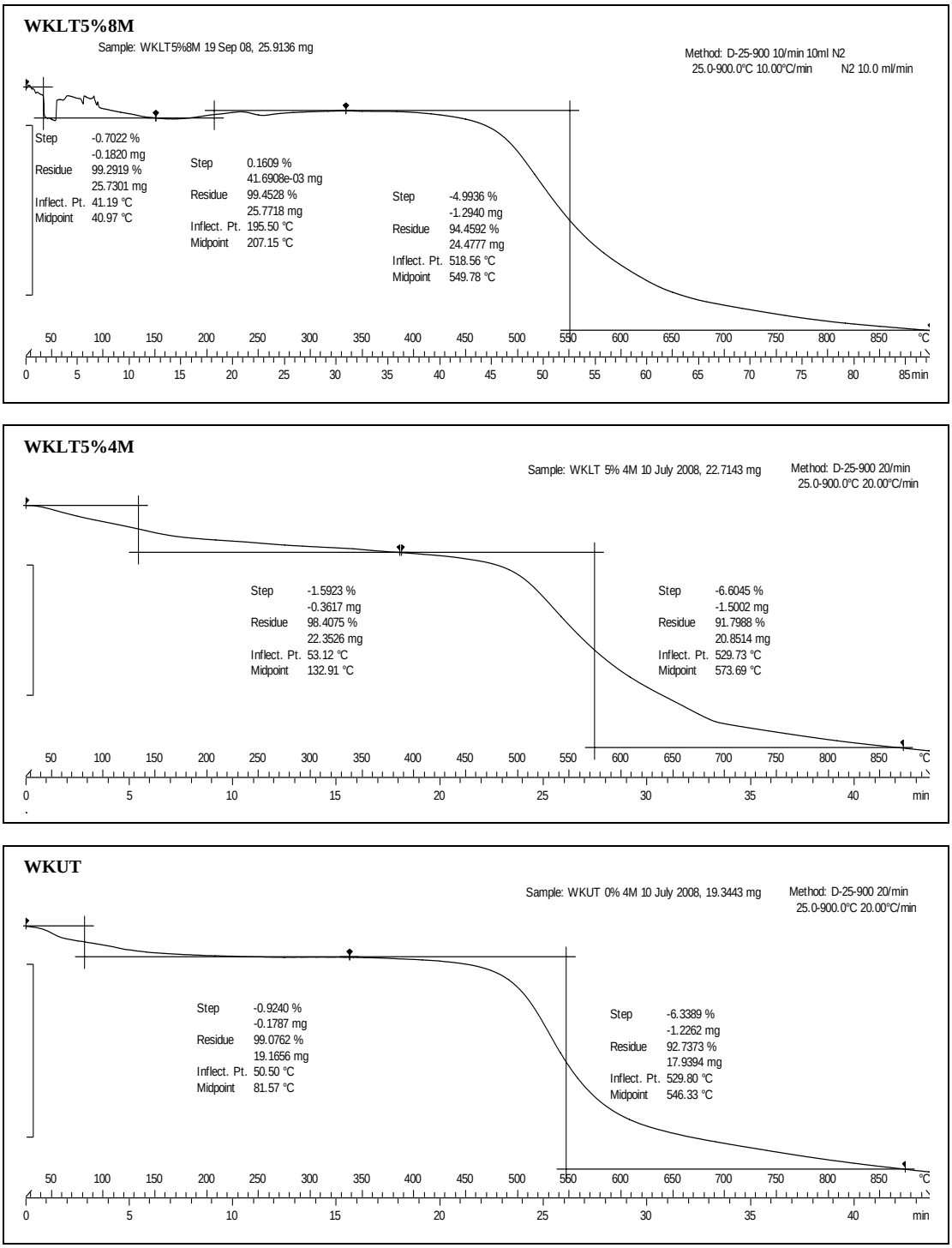


Figure 4.59 TGA spectrums of untreated and 5% lime treated White Kaolin

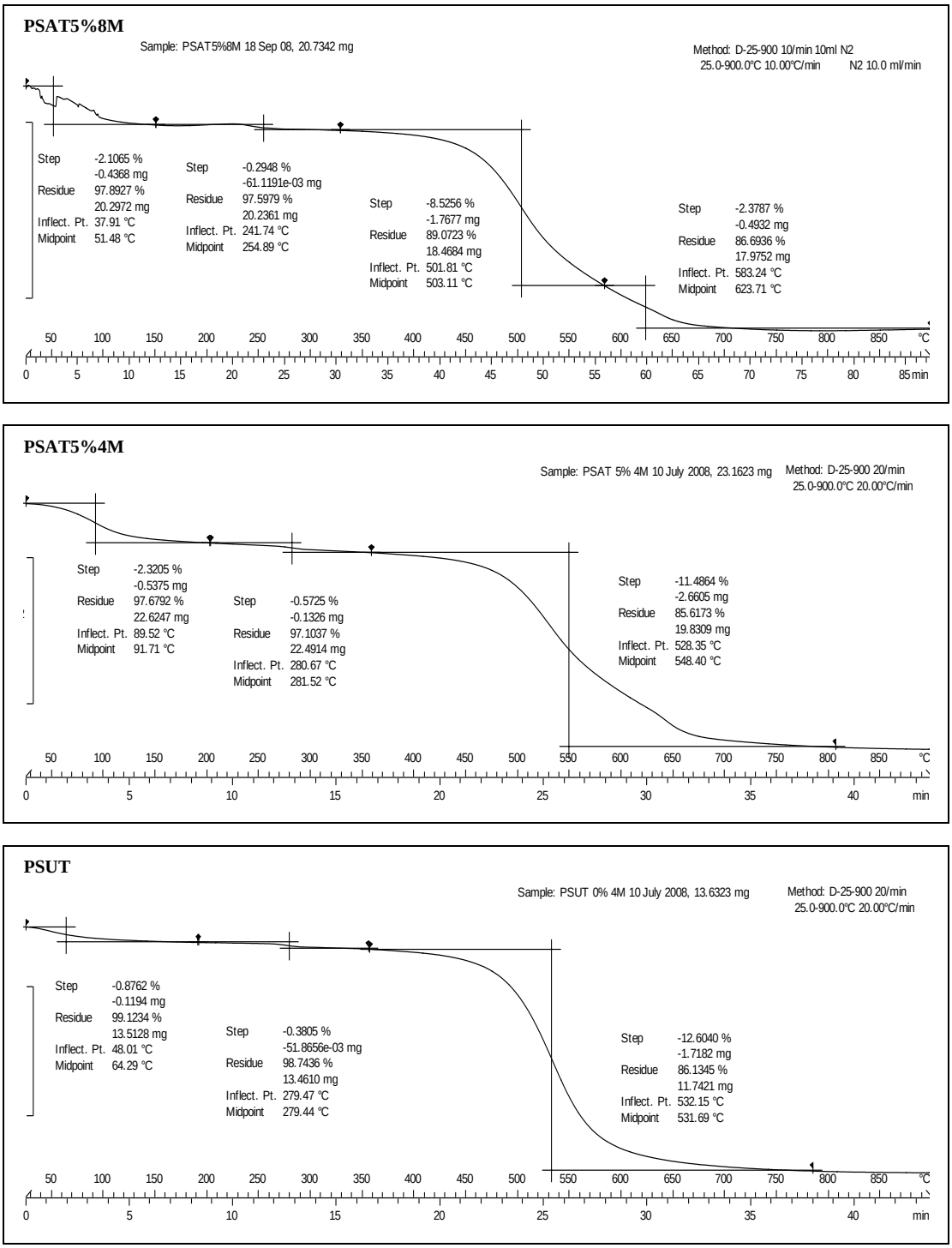


Figure 4.60 TGA spectrums of untreated and 5% phosphoric acid treated Pink Soil

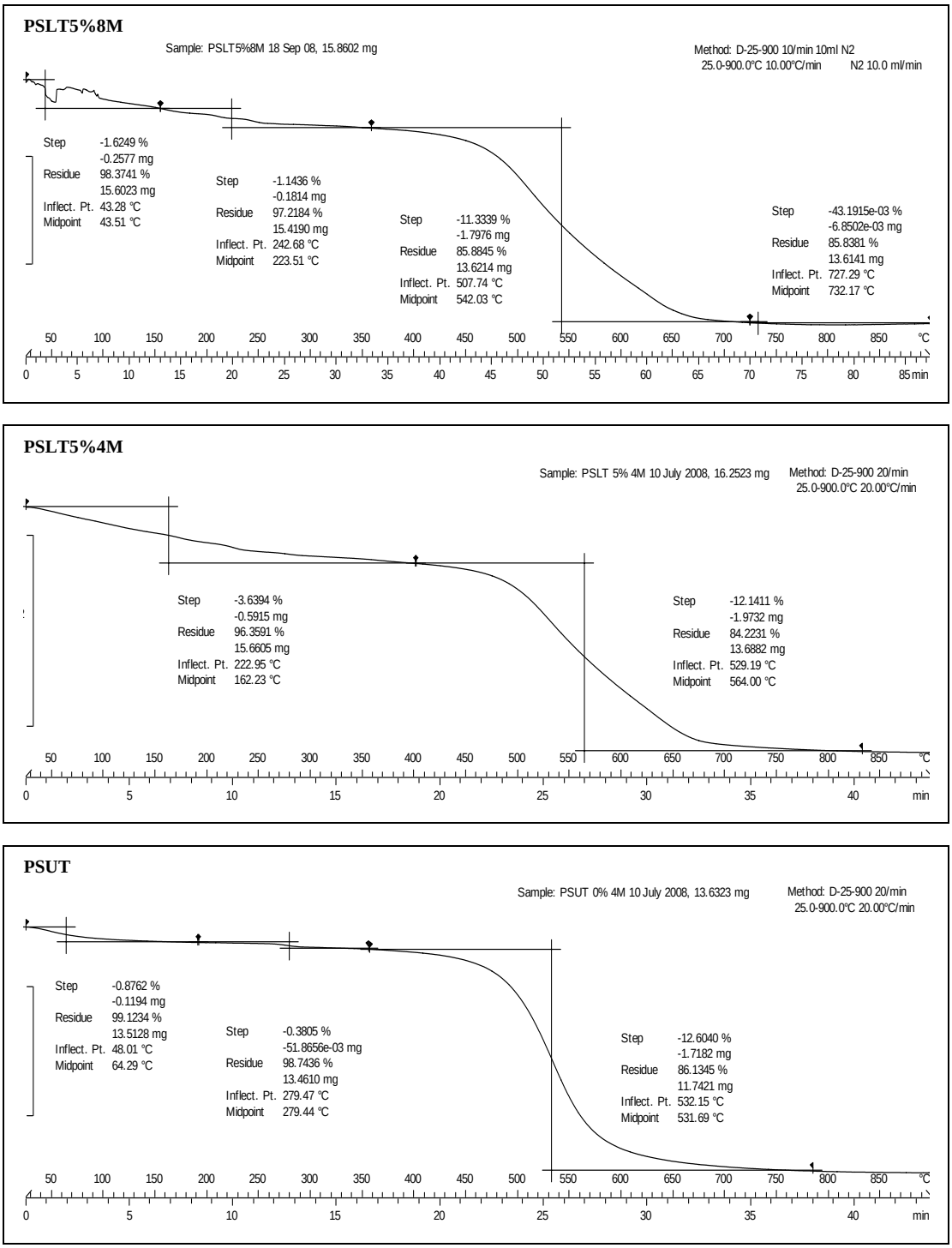


Figure 4.61 TGA spectrums of untreated and 5% lime treated Pink Soil

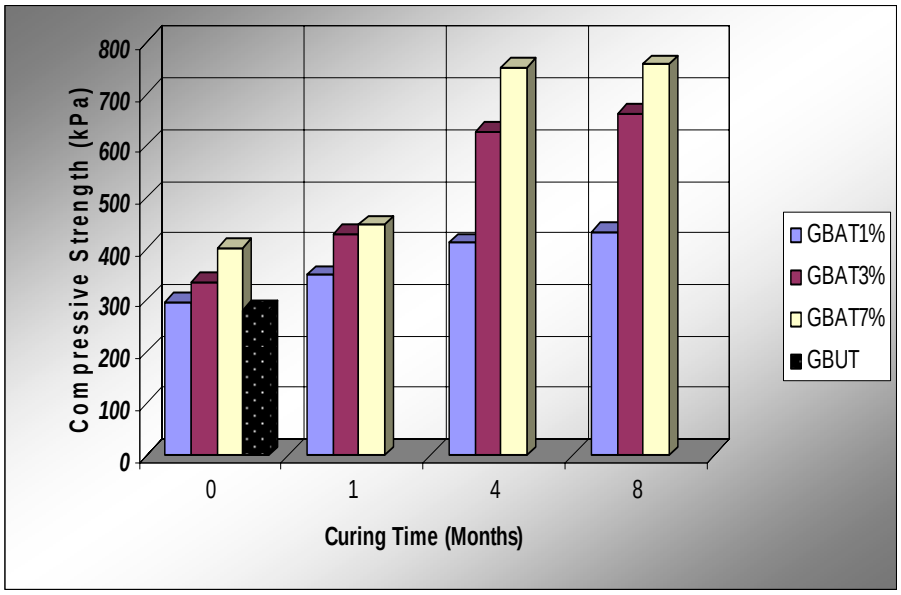
4.5 Physical Analysis of Cured Samples

4.5.1 UCS Results

Figure 4.62 shows the unconfined compressive strength of phosphoric acid and lime treated Bentonite soil under different stabilizer content and curing time conditions. It was clear that both stabilization techniques were effective in improving the strength properties of the soil. Nevertheless, the lime treatment showed the most promising results by achieving the highest compressive strength for all curing periods. For instance, at 10% lime content, the strengths increased from 1023kPa to 3082kPa over an 8 months time interval. This indicated an increase of approximately 11.4 times in comparison to the strength of natural soil (281kPa). On the other hand, following the acid treatment, where an amount of 7% by weight of the soil was incorporated into the mix design, compressive strength of 758kPa after 8 months time period was obtained which was 2.8-fold higher than the untreated sample.

Consideration on the effects of curing time also revealed some interesting points. In the acid treated samples, increasing the curing period from 4 to 8 months resulted in a marginal rise in the amount of strength gain. Whereas for samples containing 10% lime, the strength increased by almost 21% in the last 4 months period. The latter was due to the presence of free calcium ions which promoted pozzolanic reactions.

It should be stressed that the observed strength increments at the early stages of curing was largely attributed to the textural modifications caused by the ion exchange reactions. Whereas, the longer term strength developments was more reliant upon the interaction between the free stabilizers ions present in the pore water and the released clay alumina and silica. This resulted in the formation of cementitious compounds which bonded the soil particles together.



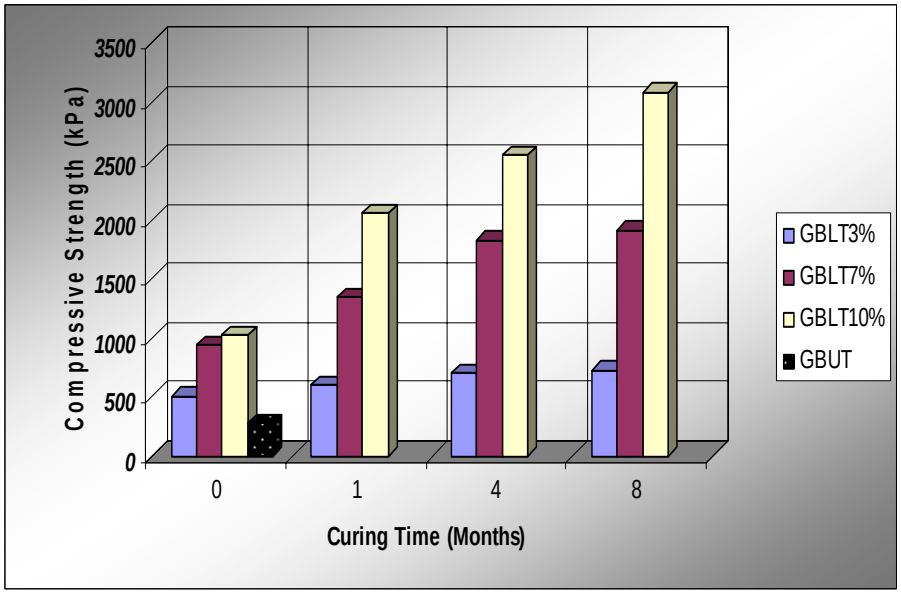


Figure 4.62 Strength development for Green Bentonite mix designs with curing time

The unconfined compressive strength of acid and lime stabilized Laterite Clay at different time intervals are shown in Figure 4.63. It was apparent that in overall the phosphoric acid treatment was more effective in improving the strength characteristics of the natural soil. As can be seen, after 8 months, the compressive strength of 7% phosphoric acid treated samples increased from 356kPa to 843kPa in comparison to the 633kPa achieved for the same amount of lime. The former was attributed to the reactions between the free phosphate ions present in the soil medium and the released clay alumina that resulted in the formation of aluminate phosphate hydrate compounds that bonded the soil particles together. Furthermore, the cementitious compounds that were formed at the early stages of curing also contributed to this increase. These new products were believed to have been formed via the exothermic reactions between the phosphate ion and the free iron and aluminum oxides present on the surface of clay particles.

In contrast to the acid treatment, at the last 4 months of curing, a marginal gain in the strength of lime mix designs was observed. Whereas, for samples containing 7% phosphoric acid, the strength raised by approximately 40% in this period. The coating action of free oxides which impeded the progression of pozzolanic reactions was believed to be the main reason responsible for this type of behavior. In general, the observed strength levels are promising to those required for road construction works, but lower than would be required for structural applications.

In order to assess the degree of improvement in the White Kaolin soil, UCS test was performed on phosphoric acid and lime treated samples. Analysis of the data presented in Figure 4.64 revealed several interesting points. First of all, the lime mix designs obtained higher strength developments for all time intervals. Secondly, after 8 months of curing, with respect to 5% lime and phosphoric acid treatment, an increase of almost ten and fivefold in the strength of stabilized soil in comparison to the natural soil were observed. The third point worth noting was the fact that for the 2% lime treated samples there was only a small gain in the strength from 4 to 8 months curing. This was caused by the lack of free calcium ions present in the soil environment to promote pozzolanic reactions. Finally, considering the effects of curing time it was also evident that with further curing there was a significant

improvement in the strength of 5% acid and lime stabilized samples. This could be explained by the slow nature of soil-chemical reactions which were mainly responsible for the formation of new reaction products that cemented the clay particles together.

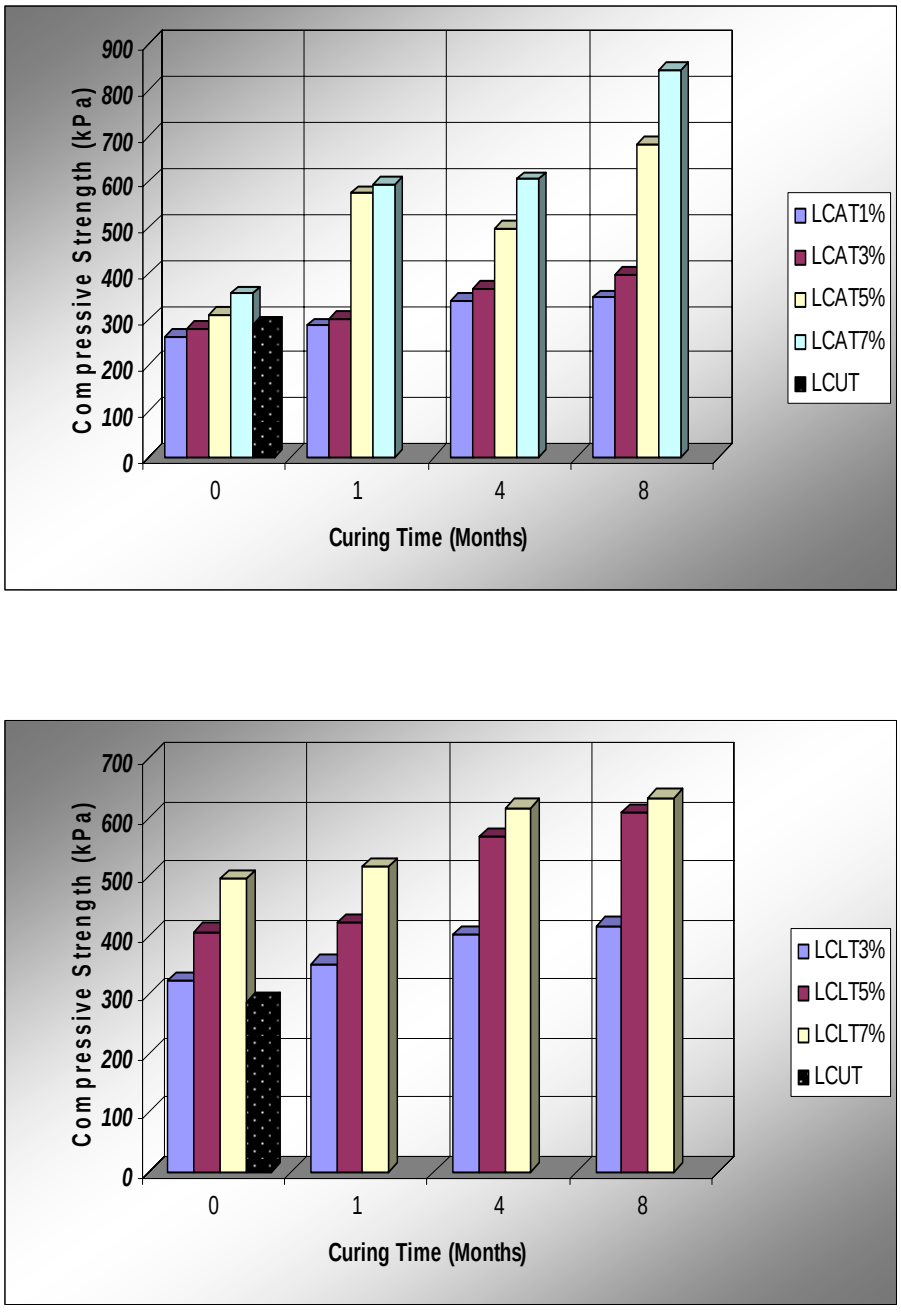
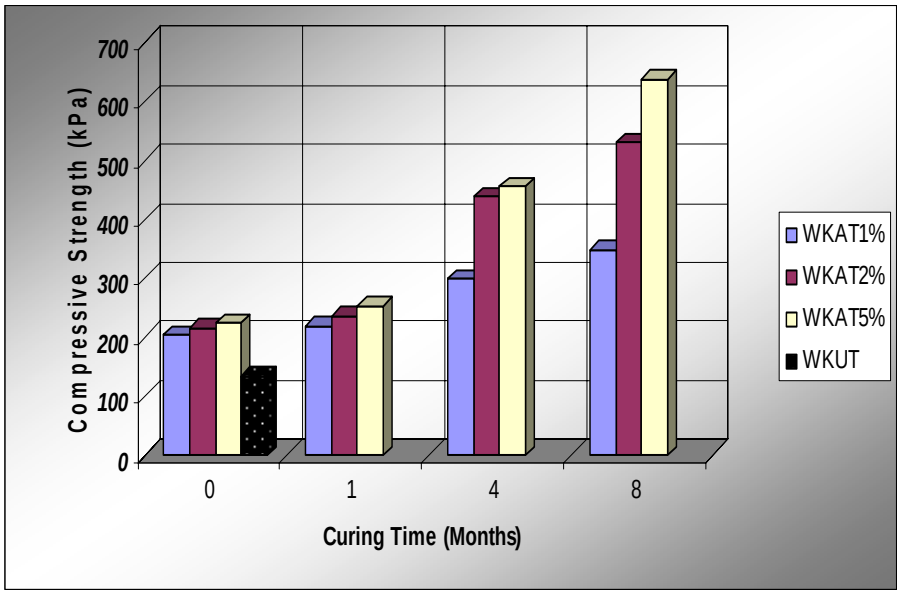


Figure 4.63 Strength development for Laterite Clay mix designs with curing time



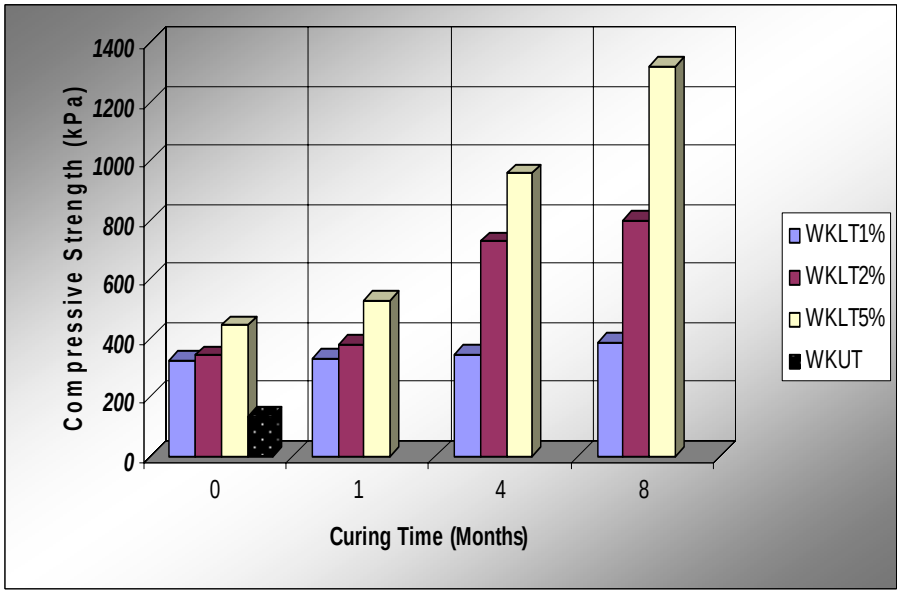
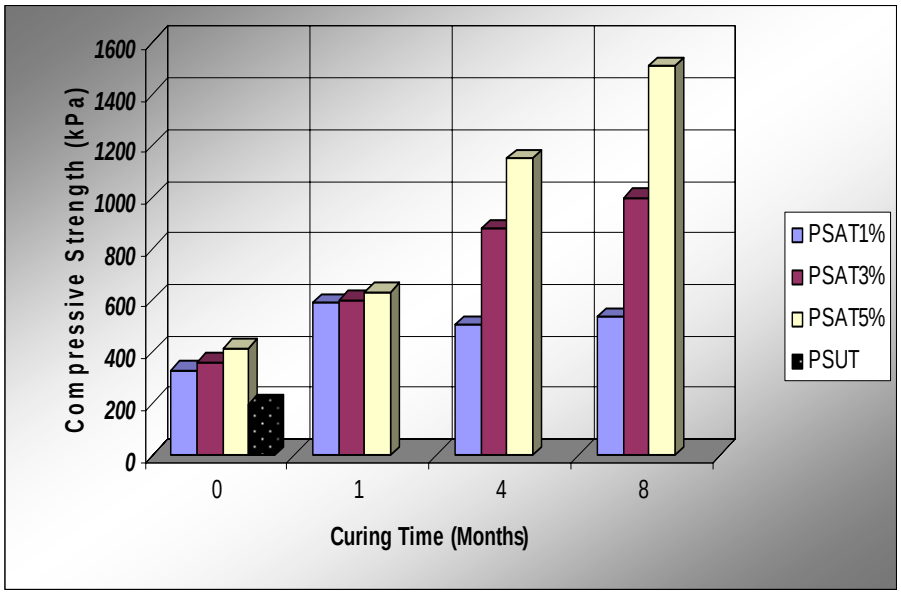


Figure 4.64 Strength development for White Kaolin mix designs with curing time

In Figure 4.65, the unconfined compressive strength of untreated and Pink Soil treated with 1%, 3%, and 5% phosphoric acid and lime are presented. As can be seen, cylindrical specimens of 5% acid treated samples attained an unconfined compressive strength of 415 to 1509kPa, over 8 months curing period. With 1% acid the strengths varied from 327 to 535kPa for the same time interval. This clearly indicated on the importance of stabilizer ions concentration in order for the stabilization technique to succeed. On the other hand, it was clear that the strengths of lime treated samples were much higher than acid mix designs. For instance, at 5% lime content, the strengths reached a value of 3155kPa after 8 months of curing. This indicated an increase of approximately 16-fold in comparison to the strength of natural soil.

It worth to note that, in comparison to the early stages of curing, increasing curing time from 1 to 8 months resulted in a much lower gain in the compressive strength of all lime mix designs. This was probably due to the rapid consumption of calcium ions in the soil-lime reactions. On the other hand, the longer term strength development for acid treated samples was likely to be more reliant upon the slow weathering action of acid on the clay structure and the subsequent formation of reaction products.



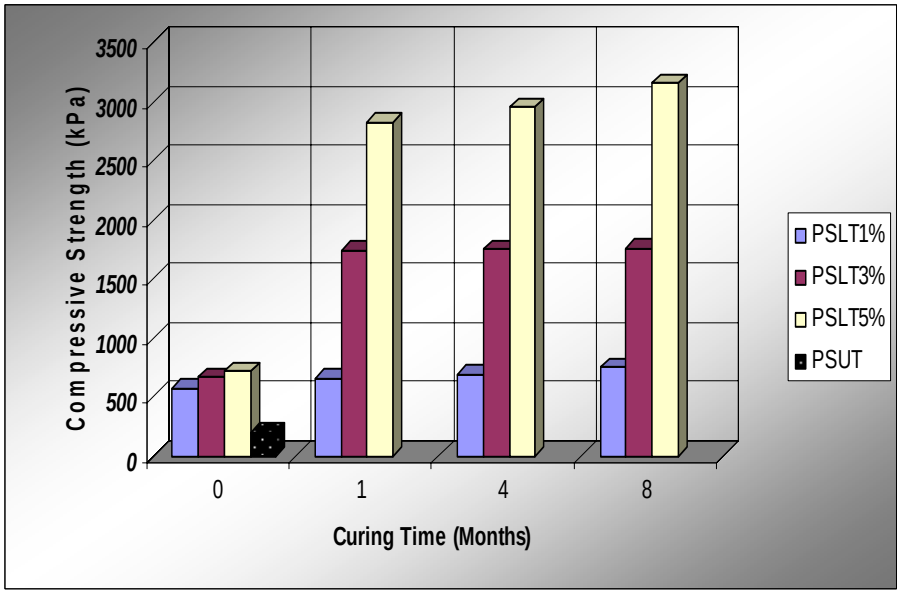


Figure 4.65 Strength development for Pink Soil mix designs with curing time

4.5.2 BET Surface Area Results

The specific surface area is an important property in assessing the physical interaction of clayey soils with chemical stabilizers. The BET results of untreated and treated Green Bentonite are presented in Figure 4.66 (refer to **Appendix F** for samples of data obtained from BET analysis). As shown, after 1 month of curing, the flocculation of soil fabric to larger clay particles gave rise to a material with lower surface area. This was caused by substitution of exchangeable ions with H^{+} and Ca^{+2} introduced by the stabilizers to the soil environment. With further curing, a sharp increase in the surface area of acid stabilized soils was observed which resulted even in a relatively higher surface area than the natural soil after 8 months of curing. The latter was attributed to the partial degradation of clay structure and the subsequent formation of new crystalline particles. On the other hand, for lime stabilization, the time-dependent changes in the surface area were negligible. Based on the high compressive strength data and FESEM images obtained for 10% lime treated samples, it could be suggested that the transformation of the film-like natural soil to a more flocculated material with different physical properties and also the blockage of pores with the new formed reaction products were the main limiting factors.

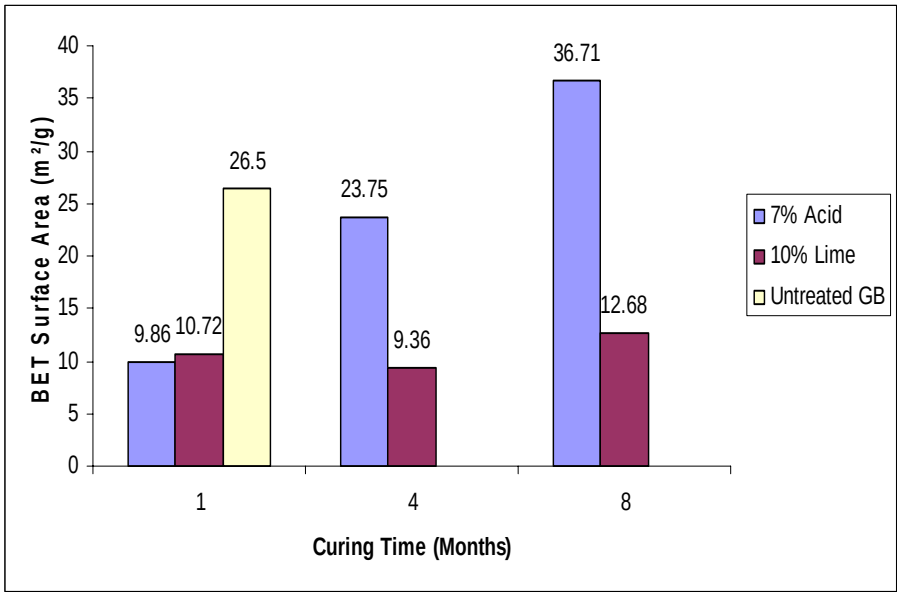


Figure 4.66 BET results for phosphoric acid and lime treated Green Bentonite samples at different time intervals

Surface area measurements for phosphoric acid and lime treated lateritic soil at 1 month, 4 months, and 8 months curing period are presented in Figure 4.67. Based on the BET results, the soil fabric showed a slightly similar trend for both mix designs. Furthermore, it seemed that the presence of free oxides as part of soil's secondary constituents, contributed to obtaining higher surface area values (Feller *et al*., 1992). As shown, after 1 month of curing, due to the fact that clay particles were heavily coated and protected by these oxides, the changes in the surface area were marginal. After 4 months of curing, a reduction in the surface area of phosphoric acid and in particular lime treated samples was observed. On the other hand, with further curing, a considerable rise in the BET surface area of lime treated samples was evident. This was probably due to the action of lime in increasing the number of accessible pores among the clay particles, as was observed in the FESEM images of 8 months cured samples. It should be noted that, the pore blockage caused by the new formed reaction products was regarded to be the major contributing factor in limiting the amount of surface area increments in the acid treated samples.

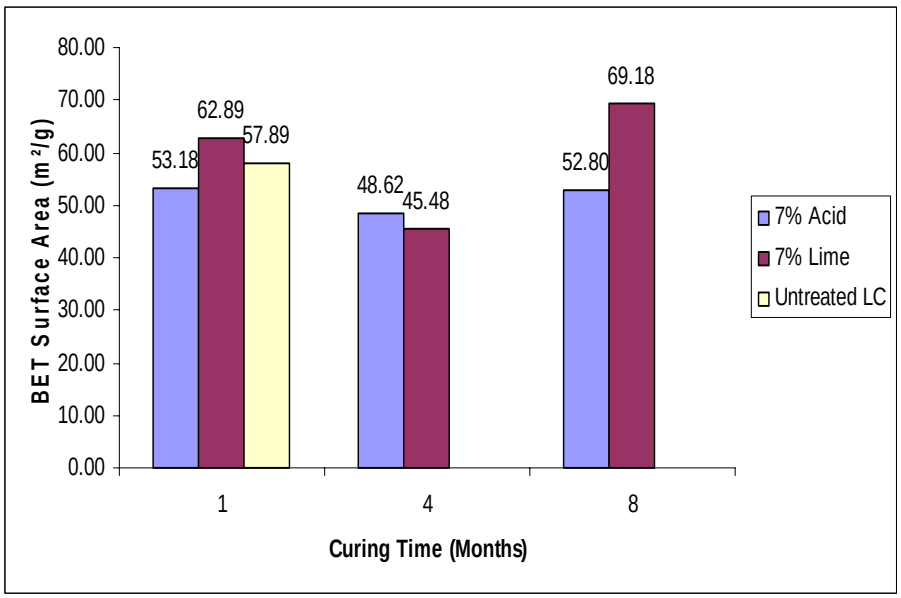


Figure 4.67 BET results for phosphoric acid and lime treated Laterite Clay samples at different time intervals

As clearly indicated from the BET results shown in Figure 4.68, the acid and lime treated White Kaolin samples revealed a sharp reduction in the surface area at the early stages of curing. This was tentatively caused by the ion exchange reactions between H^{+} and Ca^{+2} introduced by the stabilizers and the kaolinite mineral exchange sites which rendered a material with larger particles. However, after 4 months, due to the partial degradation of the clay structure, a significant increase in the surface area of lime stabilized soil was observed, while declining at the later stages of curing. The re-crystallization of the reaction products was believed to be the main mechanism responsible for this decrease. On the other hand, the acid treated samples retained their low surface area values for all curing periods. This indicated the transformation of the natural soil to a completely new material.

In Figure 4.69, the results of a series of BET nitrogen analysis on the surface area of lime and phosphoric acid treated Pink Soil is illustrated. From graphs, it was evident that the surface area variations in both mix designs followed a similar pattern.

At the early stages of the acid treatment, the substitution of exchangeable cations with the H^{+} ion gave rise to a material with lower surface area values. These changes in the lime treated samples were negligible. With further curing to 4 months, a sharp increase in the surface area of both mix designs due to the partial degradation of the octahedral layer was observed. However, at 8 months time interval, a reduction in the surface area of lime and phosphoric acid treated samples was apparent. The pore blockage caused by the re-crystallization of the cementitious compounds was regarded to be the main contributing factor to this decrease.

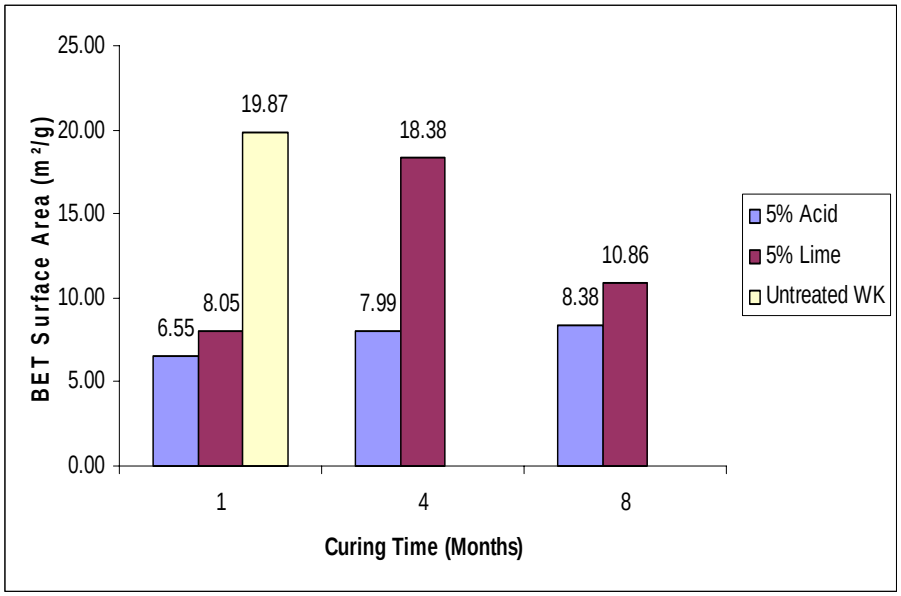


Figure 4.68 BET results for phosphoric acid and lime treated White Kaolin samples at different time intervals

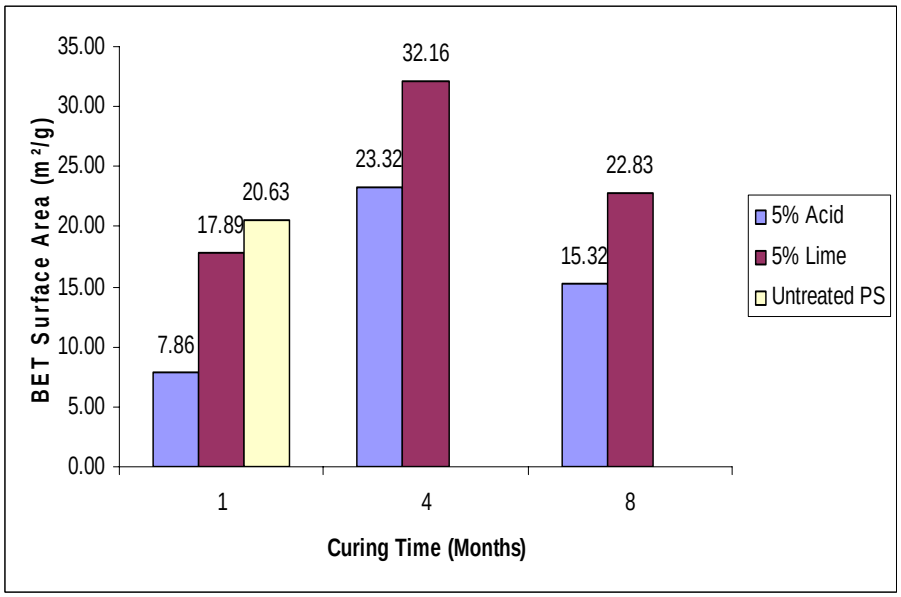


Figure 4.69 BET results for phosphoric acid and lime treated Pink Soil samples at different time intervals

4.6 Summary

In this investigation, a variety of analytical techniques that were linked to the micro-structural, molecular and leaching characteristics of the soil were performed on lime and phosphoric acid treated mix designs. This was carried out in an attempt to identify the mechanisms that contributed to the stabilization process. The summary of obtained results is discussed in the following paragraphs.

In Green Bentonite samples, on addition of 1% and 7% phosphoric acid, the level of soluble P and Al in the aqueous solution reached a maximum after 4 months curing period. However, with further curing, a reduction in the concentration of soluble Al and P were observed. This was explained via the re-crystallisation process of reaction products which were mainly comprised of these elements. On the other hand, in lime mix designs, the level of soluble Si was much higher than the soluble Al concentrations which remained quite low for all curing periods. This was due to the fact that the majority of edge sites in montmorillonite minerals were associated with the tetrahedral silicate structure. Also, similar to phosphoric acid treatment, with increasing curing time to 8 months, the soluble Ca plot revealed a downward trend in the level of Ca released to the solution. This was consistent with the incorporation of Ca into reaction products.

The release of soluble Al, Si, P or Ca with respect to phosphoric acid and lime treatment for White Kaolin, Pink Soil, and Laterite Clay mix designs were also presented in this thesis. As was seen in the lime stabilized soil, with increasing curing time there was a sharp reduction in the level of Ca monitored in the aqueous solution. This was consistent with the incorporation of Ca ion into the reaction products. On the other hand, the phosphoric acid treated samples revealed virtually a similar trend for all curing periods with an optimum at 4 months time interval. This behavior confirmed the formation of inner-sphere complexes between the phosphate ion and the surface hydroxyl groups at the early stages of curing (1 month). With further curing to 4 months, an increase in the level of soluble P was observed. This was caused by the weathering action of acid on the soil structure. It should be noted that the reduction in the level of soluble P at longer curing periods was consistent

with the formation of new reaction products which rendered them less soluble. In addition, in Laterite Clay samples, comparison between the soluble concentration of Al element in both phosphoric acid and lime mix designs revealed some interesting points. First of all, the Al release for 7% acid treated samples seemed to increase with curing time while in contrast, the Al concentration of solutions stabilized with lime showed a significant decrease, with a sharp reduction occurring after 4 months. The former can be attributed to the highly acidic nature of pore water which resulted in the dissolution of clay alumina and the free aluminum oxides present in the soil environment. While the latter was likely to be caused by the coating action of free oxides and their lower dissolution in an alkaline environment which prevented the attack of lime on the clay mineral structure.

XRD graphs of phosphoric acid and lime treated samples after 1, 4, and 8 months of curing were studied in this research. As was seen, the major clay minerals present in the natural soil were montmorillonite ($2\theta \approx 8^o$, 21^o, 28^o, 35^o, 62^o), illite ($2\theta \approx 9^o$, 22^o, 42^o), kaolinite ($2\theta \approx 12.5^o$, 18.5^o, 20^o, 36^o, 63^o), quartz ($2\theta \approx 21.5^o$, 25^o, 38^o), geothite ($2\theta \approx 18.2^o$, 21.8^o), and calcite ($2\theta \approx 29.4^o$, 43.2^o). The qualitative analysis of the XRD results for Green Bentonite samples indicated that in contrast to lime treatment, after application of the acid, the characteristic peaks of montmorillonite ($2\theta \approx 8^o$) and illite ($2\theta \approx 9^o$) appeared to have vanished. These alterations suggested that a partial destruction in the structure of montmorillonite and illite have occurred. For Laterite Clay samples, no fundamental changes in the XRD patterns of acid and lime treated samples were observed. On the other hand, for chemically treated White Kaolin samples, all intensities of kaolinite mineral reflections decreased with time. Furthermore, several new reflections regarding the formation of new products at various 2θ angles were observed.

As was seen from the EDAX spectrums, aluminum, silicon, phosphorus, and calcium peaks were clearly evident in the soil mix designs. Also, in Laterite Clay samples, the high concentration of iron (Fe) element confirmed the lateritic nature of the soil and moreover the presence of free iron oxides on the surface of clay particles.

Comparison of the EDAX results for the Al:Si ratio of untreated, phosphoric acid and lime treated Bentonite samples did not yield significant changes with curing time. In Laterite Clay samples, the Al:Si ratio varied less than 10% between various mix designs. However, a considerable increase in the Al:Si ratio of White Kaolin samples after 4 months of curing was obsereved. The latter was consistent with a mechanism in which compounds of aluminate hydrate gels were deposited on the surface of clay particles.

As was expected, the FESEM images of untreated Green Bentonite and White Kaolin samples showed a dispersed film-like and neatly arranged book-like microstructure, respectively. The presence of needle shaped gypsum minerals in the Pink Soil medium was also observed. On the other hand, in chemically treated Bentonite samples, the soil fabric was transformed from a flake based form into a more flocculated structure. For Laterite Clay mix designs, it was apparent that at the early stages of curing, no appreciable changes in the soil texture had occurred. However, with increasing curing period, the vigorous action of acid on clay minerals and in particular the free oxides, transformed the soil structure into a more integrated composition consisting of sharper edged particles. A similar textural pattern was also observed in lime and phosphoric acid treated White Kaolin and Pink Soil mix designs.

In this research, the FTIR spectra for natural and chemically treated soils in the middle-infrared region (400–4000 cm^{-1}) were obtained. As was seen, the KBr curve of untreated Green Bentonite was characteristic of montmorillonite mineral with a single sharp band at 3632 cm^{-1} followed by a broad band at 3446 cm^{-1} for OH stretching of structural hydroxyl groups and water, respectively. In Laterite Clay, White Kaolin, and Pink Soil the presence of kaolinite mineral with strong bands at different wavelength (cm^{-1}) was apparent. There were also some quartz present as indicated by the bands at 778 cm^{-1} and 791 cm^{-1}.

Assessment of the FTIR spectrums in phosphoric acid and lime treated samples also indicated few noticeable changes. First of all, there was a slight decrease in the intensity of some bands such as AlAlOH with curing time. These

changes were probably caused by the action of stabilizers on the clay structure. Secondly, in 8 months cured Bentonite samples, a new peak at 2920 cm^{-1} due to phosphoric acid treatment was evident. Furthermore, a new absorption band at approximately 1385 cm^{-1} to 1420 cm^{-1} for different lime mix designs was observed. This peak was tentatively assigned to the Ca–OH bond of lime present in the soil medium.

^{27}Al and ^{29}Si MAS NMR spectroscopy were performed on untreated and 8 months cured Green Bentonite and Laterite Clay samples. The test was carried out in order to determine the local structure around the Al and Si atoms and also to further elucidate the stabilization process. In contrast to the Laterite Clay samples, the ^{27}Al NMR spectrum of the natural Bentonite soil revealed a relatively sharp symmetric band at approximately 57ppm corresponding to the tetrahedrally coordinated Al, and a small peak at 2ppm arising from octahedral Al. For 8 months cured samples, the same tetrahedral peak to the original peak for the stabilized samples were observed. Nevertheless, there was a slight difference in the value and the intensity of octahedral Al peaks.

In the ^{29}Si MAS NMR spectrum of the natural Bentonite soil, a peak at -94ppm corresponding to the tetrahedral layers of clay silica and a sharp peak at -108.5ppm suggesting the presence of quartz mineral were evident. Also, some changes in the structure of clay minerals due to addition of lime and the presence of a new peak at about -84ppm corresponding to the Q_2 structure were apparent. On the other hand, in Laterite Clay samples, after 8 months of curing, a narrower and more intense peak at −92ppm was observed.

The acidic nature of untreated Laterite Clay, White Kaolin, and Pink Soil samples was confirmed with the low pH value obtained for these soils. In contrast, an average pH value of 9.03 (alkaline) was obtained for the untreated Bentonite soil. As was seen, the pH value of the solution reduced sharply for phosphoric acid treated samples, while, revealing a significant rise for lime mix designs. Also, with increasing curing period, the pH for lime and acid treated samples showed a decrease and an increase in its value, respectively.

It was evident from the graphs that after 1 month of curing, lime treatment caused a noticeable increase in the CEC_p value of soil samples. This was probably due to an increase in OH^- ion concentration of pore water and development of more negative charges on the surface of clay particles. At 4 months time interval, a reduction in the CEC_p values of both design mixes was observed. However, with further curing, the increase in number of broken bonds around the edges of particles in the soil-stabilizer matrix and moreover the formation of reaction products that acquired negative charges contributed to the CEC_p of the material, thus increasing the CEC_p value at 8 months curing period.

The TGA curves for treated Green Bentonite indicated that the soil dehydration covered the temperature ranges between 72ºC to 231ºC, with the maximum dehydration occurring at 105ºC for 4 months lime treated samples. This weight loss was due to the evaporation of the adsorbed water on the surface and inter-layer of montmorillonite minerals. In Laterite Clay samples, considerable amounts of organic matter were present as indicated by weight losses at temperatures around 300°C. Furthermore, in both of Bentonite and White Kaolin design mixes, a drop at approximately 250ºC to 270ºC was observed. This was tentatively caused by the evaporation of moisture encapsulated in the crystallized reaction products. The losses at approximately 650ºC and 515ºC observed in Bentonite and Laterite Clay samples was attributed to the dehydroxylation of montmorillonite and kaolinite minerals, respectively.

The unconfined compressive strength of phosphoric acid and lime treated soil samples under different stabilizer content and curing time conditions were studied in this research. In 8 months cured Bentonite samples, on addition of 10% lime, the strengths indicated a rise of approximately 11.4 times in comparison to the natural soil. On the other hand, at 7% acid content, the strengths increased to 758kPa over an 8 months time interval which was 2.8-fold higher than the untreated sample.

In Laterite Clay samples, it was clear that the phosphoric acid treatment was more effective in improving the strength properties of the soil. That is, after 8 months of curing, the compressive strength of 7% phosphoric acid treated samples increased from 356kPa to 843kPa in comparison to the 633kPa achieved for the same lime content. Furthermore, in contrast to the acid treatment, at the last 4 months of curing, a marginal gain in the strength of lime mix designs was observed. Whereas for samples containing 7% phosphoric acid, the strength raised by approximately 40% in this period.

In White Kaolin samples, with respect to 5% lime and phosphoric acid treatment, an increase of almost ten and fivefold in the strength of 8 months cured samples were observed. Similar to Green Bentonite and White Kaolin soil, it was clear that the strengths of lime treated Pink Soil samples were much higher than phosphoric acid mix designs. That is, at 5% lime content, the strengths reached a value of 3155kPa after 8 months time interval. This indicated an increase of approximately 16-fold in the strength of natural soil.

In general, the BET surface area of treated samples revealed a reduction at the early stages of curing. This was caused by the substitution of exchangeable ions with H^{+} and Ca^{+2} introduced by the chemical stabilizers to the soil fabric. With further curing to 4 months, a rise in the surface area of stabilized soils was apparent. The latter was attributed to the partial degradation of the clay structure. On the other hand, in Laterite Clay samples, a reduction in the surface area of phosphoric acid and in particular lime treated samples was observed for this period. After 8 months of curing, in contrast to Green Bentonite and Laterite Clay samples, a reduction in the surface area of White Kaolin and Pink Soil mix designs was observed. The pore blockage caused by the re-crystallization of the cementitious compounds was regarded to be the main contributing factor to this decrease. Also it was suggested that the action of lime in increasing the number of accessible pores among the clay particles was the main cause of increase in the BET surface area of Laterite Clay samples at the later stages of curing.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Lime and Phosphoric Acid Stabilization Mechanisms

This research was carried out in order to fulfill two main objectives. First of all, the introduction of phosphoric acid as a non-traditional stabilizer and secondly, to identify and elucidate the mechanisms by which clayey soils are modified and stabilized under acidic and basic conditions. The latter was achieved by collecting data from various analytical techniques that were linked to the micro-structural, molecular, and leaching characteristics of the treated soil. In chapter 4, based on the physico-chemical behavior of each individual soil type, these results were discussed comprehensively. This chapter will present the main significant conclusions of that discussion and on the basis of those conclusions proposals for further research will be recommended.

5.1.1 Time-Dependent Changes in Pore Water Chemistry

As was seen, in lime treated Green Bentonite samples, soluble Si was the main element released into the aqueous solution in contrast to the more prominent soluble Al observed in other lime mix designs. Since Laterite Clay, White Kaolin, and Pink Soil samples were comprised mainly of kaolinite mineral, it could be

suggested that this behavior was due to the 2:1 layer structure of montmorillonite mineral and the fact that the source of alumina was sandwiched between the two silica layers. In addition, the hydroxyl groups exposed at the surface of kaolinite particles were strongly pH sensitive. Therefore at high pH, there was a greater tendency for H^+ from the hydroxyls to go into the solution. This tendency in turn initiated mineral dissolution directly next to a source of alumina in the clay structure. On the other hand, at low pH since the hydroxyl sites became positively charged the clay alumina was released from surface sites by protonation action.

In general, at the early stages of curing, due to the slow weathering nature of the stabilizers, the reactions were mostly associated with the ion exchange effects alone. However, with increasing curing time, the chemical reactions were based on Al and Si dissolution from the respective minerals. The latter was observed in both of the Green Bentonite and White Kaolin mix designs. On the other hand, in lime treated Laterite Clay samples, soluble Al release decreased with curing time, indicating that lime treatment did not result in major dissolution of clay alumina but only the free aluminum oxides. Nevertheless, in phosphoric acid treated samples, Al concentration increased linearly with curing time, suggesting a chemical weathering of the clay structure.

At 8 months time interval, the level of soluble Ca and P reduced significantly for all design mixes. This was due to the incorporation of stabilizer ions into the cementitious compounds which rendered them less soluble. This behavior was also observed in the levels of soluble Al and Si obtained from the aqueous solution. The latter confirmed the presence and role of clay alumina and clay silica in the formation of new reaction products.

5.1.2 Micro-Structural Developments

Based on the XRD results obtained from chemically treated Green Bentonite samples, a slight decrease in the intensity of montmorillonite peaks was observed. Furthermore, in phosphoric acid mix designs, the characteristic peaks of montmorillonite ($2\theta \approx 8^{o}$) and illite ($2\theta \approx 9^{o}$) seemed to have vanished. These alterations suggested that some sort of partial destruction in the structure of clay minerals had occurred. On the other hand, in White Kaolin soil, intensities of kaolinite mineral reflections decreased with time. This was consistent with the vigorous action of acid on the clay structure and also the highly pozzolanic behavior of kaolinite in an alkaline environment. Furthermore, comparison of the XRD patterns for 8 months cured mix designs revealed several new peaks at various 2θ angles. The peaks were tentatively assigned to phosphate hydrate and calcium hydrate compounds in the acid and lime treated samples, respectively. These findings were consistent with the fact that, phyllosilicates are the principal minerals that are attacked in an acidic and basic environment and consequently, they are the primary source of alumina and silica required for the formation of new products.

In the EDAX spectrums of various soil types, aluminum (Al) and silicon (Si) peaks were clearly evident in the untreated and treated samples. The presence of both of these elements along with their intensity confirmed the dominancy of clay minerals in the soil medium. In addition, with respect to phosphoric acid and lime treatment, soil samples also contained phosphorous (P) and calcium (Ca). The latter was consistent with the presence of phosphoric acid and lime stabilizers in the soil medium.

As was noticed by the P:Si and Ca:Si ratios of different soil types, there were a appreciable change in the surface composition of clay particles which emphasized on the fact that some sort of chemical reactions were taking place. Since with the exception of lime treated Bentonite samples, Si was not attacked by the stabilizer ions, the increase in the P:Si and Ca:Si ratios was tentatively assigned to the development of a gel compound micro-structure containing stabilizer ion on the surface of clay particles. On the other hand, the crystallization of the new formed

products into the pores of clay particles and/or an increase in the sources of silica exposed at the surface of clay particles were believed to be the main cause of relatively lower P:Si and Ca:Si ratios of various lime and phosphoric acid design mixes.

The FESEM images of chemically stabilized soils indicated that the morphological changes induced in the soil-lime matrix were similar to that observed in phosphoric acid treated samples but with a stronger or weaker intensity. In other words, the flocculation and the weathering of soil particles with respect to the release of stabilizer ions and the subsequent chemical reactions rendered a more aggregated structure containing clay-stabilizer clusters and sharp-edged particles. Furthermore, for most of the 8 months cured design mixes, the formation of new reaction products in form of white lumps was evident.

5.1.3 Monitored Molecular Structure

From a molecular perspective, as was seen in the NMR spectra, the ^{27}Al NMR revealed the same tetrahedral peak to the original peak for the stabilized samples. Furthermore, it was found that the Al present in the octahedral layer of clay minerals were more amenable to chemical attacks and also partly responsible for the formation of new products.

According to ^{29}Si NMR results, the addition of lime to Green Bentonite samples seemed to bring some noticeable changes to the structure of clay particles present in the soil medium. This was attributed to the weathering action of lime on the crystalline clay structure. On the other hand, the molecular structure of the lime treated Laterite Clay samples was essentially similar to that of the natural soil. A rational explanation for this type of behavior was the fact that most of the attacks by lime were confronted with the free oxides that coated the surface of soil particles, therefore, preventing major changes in the tetrahedral and octahedral sites of clay minerals.

The FTIR spectrums of treated samples suggested that the chemical stabilizers did not cause any major alterations in the molecular structure of clay particles. However, there were slight decreases in the intensity of some bonds with curing time. On the other hand, in lime mix designs, a new absorption band attributed to the Ca–OH bond of lime present in the soil medium was evident.

5.1.4 Characteristics of the Soil-Stabilizer Matrix

From pH measurements conducted on various soil types, it was evident that the differences in pH value of treated samples due to the type of treatment were significant. It was also clear that as the amount of stabilizer ions had a profound impact on the pH of pore water and hence the solubility of the elements as was seen in the leaching test results. Furthermore, with the progression of time, it was found that the pH value in soil-stabilizer matrix showed a tendency for reaching its natural state due to the reduction of alkaline and acid ions in the pore water and also the crystallization of the new formed compounds.

In this research, cation exchange capacity caused by permanent charges (CEC_p) was measured for design mixes that showed the highest degree of improvement. As was seen, at the early stages of curing, in contrast to lime treatment, a noticeable decline in the CEC_p value of acid mix designs was observed. This was explained by the protonation action of phosphoric acid on the clay structure which limited the accessibility to the exchange sites. Whereas, in lime stabilized soils due to an increase in OH^- ion concentration of pore water, a relatively higher CEC_p values were achieved.

With further curing to 8 months, a rise in the CEC_p values of various design mixes was evident. The latter was attributed to an increase in the number of broken bonds around the edges of clay particles and also the formation of new compounds which acquired negative charges in the soil-stabilizer matrix. Also it was found that in soil types comprised mainly of kaolinite mineral, in comparison to lime treatment,

the changes in CEC_p value of acid treated samples were rather limited. This was because of the dependency of charges on the surface of clay particles to the pH of pore water which as was indicated by the pH results remained quite low for all curing periods.

It was seen from the TGA results that evaporation of the adsorbed surface water was the main reason responsible for the weight losses observed in the lower temperature regions. Furthermore, soil dehydration extended the temperatures up to 300ºC in some samples. This was tentatively assigned to the evaporation of moisture encapsulated in the reaction products and the inter-layer of clay minerals such as montmorillonite. Also, it was found that with the exception of Laterite Clay samples, the treatment of soils with chemical stabilizers had a negligible impact on the dehydroxylation process of clay minerals which was observed at temperature ranges between 500ºC to 750ºC.

Comparison between the BET results of the natural and chemically treated samples indicated that the effect of acidic and basic stabilizers on the surface area of soil particles were significant and rather conflicting. For instance, based on the BET results obtained for 1 month, 4 months, and 8 months cured Laterite Clay samples, the soil fabric showed virtually a similar trend for both mix designs. Furthermore, it was found that the presence of free oxides in the form of micro-aggregates contributed to achieving higher surface area values. On the other hand, in 10% lime treated Green Bentonite and 5% phosphoric acid treated White Kaolin samples, the transformation of the natural soil to a material with new physical properties was clearly evident.

In general, at the early stages of the curing, the substitution of exchangeable ions with H^+ and Ca^{+2} introduced by the chemical stabilizers lowered the surface area values. While, the partial degradation of the clay structure with curing time gave rise to a material with higher surface area values. At longer curing periods (8 months), the re-crystallization of the new formed reaction products around and into the pores of soil particles, was believed to be the major contributing factor to the changes observed in the surface area of treated samples.

5.1.5 Correlation between the Strength and the Stabilization Process

Analysis of the compressive strength data presented in this thesis and the results obtained from other analytical techniques, revealed several interesting points which are summarized below:

a) In comparison to phosphoric acid treatment, the lime mix designs for Green Bentonite, White Kaolin, and Pink Soil obtained higher strength developments for all curing periods. Whereas for Laterite Clay samples, the 8 months cured phosphoric acid stabilized soil achieved the highest degree of strength. On the other hand, in soil samples treated at lime contents obtained by the ICL test there was only a small gain in the strength from 4 to 8 months curing. This was caused by the lack of free calcium ions present in the soil environment to promote pozzolanic reactions.

b) According to the data obtained for Laterite Clay mix designs, it was found that the stabilization process is highly sensitive to the impurities present on the surface of clay particles. For instance, the coating action of free oxides was believed to have a detrimental effect on the progression of pozzolanic reactions which resulted in a marginal gain of strength at the last 4 months of curing.

c) The leaching and pH test results highlighted a very important point regarding the chemical composition of the reaction products. The fact that, in an alkaline and acidic environment, clay alumina was more liable to dissolution. Therefore, it was rational to suggest that with respect to lime and phosphoric acid treatment, aluminate hydrate compounds were more likely to be formed. Whereas, in lime treated Green Bentonite samples, clay silica was more dominant in the pore water and hence the formation of silicate hydrate compounds was more feasible.

d) In conclusion, based on the data obtained from various spectroscopic and microscopic techniques and bearing in mind the type of clay minerals and impurities present in the soil medium, it could be postulated that the primary

ion-exchange reactions followed by a surface alteration of the clay structure were the main mechanisms responsible for the improvement of lime and phosphoric acid stabilized soils. The latter was confirmed via NMR and FTIR results which indicated that the additives did not penetrate deeply within the layers of clay minerals. In addition, the Ca:Si and P:Si ratios obtained from EDAX analysis suggested that there were significant changes in the surface composition of soil particles at different time intervals. This also emphasized on the fact that the soil-stabilizer reactions were mainly surface-associated.

5.2 Recommendations

In this thesis, the reaction mechanisms of two clays comprised mainly of montmorillonite and kaolinite minerals and two tropical Malaysian soils treated with phosphoric acid and lime were investigated. Based on the results obtained from different spectroscopic and microscopic techniques, the main chemical reactions regarding the stabilization processes of various soil types were explained. Some recommendations regarding future evaluations carried out in this field are as follows:

a) As was seen, in order to monitor the concentration of stabilizer ions and the released elements, laboratory scale leaching test was performed on the pore water chemistry. Nevertheless, it is crucial to evaluate the validity of the results for the actual field conditions, with soils having higher organic contents and particularly the effects of environmental conditions such as periodic rainfalls on the time dependent soil-stabilizer reactions. This can be achieved by performing tests such as column leaching during the stabilization process.

b) As was emphasized throughout this research, the variations in water content and degree of compaction can lead to considerable changes in the arrangement of particles in the soil fabric which may in return influence the soil-chemical reactions. Hence, by preparing samples at different compactive

efforts, a rational relationship between these two parameters and the chemical changes induced can be developed.

c) In this study, unconfined compressive strength test was used as an index of soil improvement. However in order to better simulate the actual stress conditions particularly in cases where accuracy is an important priority such as mitigating landslides using stabilization techniques, the triaxial compression tests may seem to be more appropriate which can be implemented in future studies. On the other hand, leaching, EDAX, CEC_p and BET surface area analysis were found to be the most useful techniques for assessing the time-dependent changes in the chemical characteristics of treated particles. Therefore, future studies can focus more on these characteristics.

d) The finding of this research clearly pointed to the need to identify the type of minerals and impurities present in the natural soil prior to their stabilization. This is particularly relevant for the reddish lateritic soils commonly found in tropical regions which are usually heavily coated with free oxides that can inhibit the potential benefits of lime addition. It is also important to assess and develop low cost additives that can adsorb or dissolve these oxides. In addition, it would be beneficial to build a database of different impurities present in Malaysian soils as well as their chemical composition and molecular structure.

e) Finally, with the support of government agencies, specific soil sites that pose problems can become available for geotechnical engineers and researchers working in different institutions where the data obtained using different remediation techniques can be shared and evaluated among the research community. Based on the obtained results from the laboratory scaled investigation and the one obtained for the actual field conditions, a standard guideline can be developed which enables the engineers to predict the degree of improvement using various stabilizers.

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Appendix A

Leaching test results for untreated Green Bentonite

LOTUS LABORATORY SERVICES (M) SDN. BHD.
Associate of LOTUS TECHNICAL SERVICES
5 & 7, Jalan Bakawali 36, Taman Johor Jaya, 81100 Johor Bahru, Johor, Malaysia.
Tel : 07-3554063, 3556869, 3548060, 3559127 Fax : 07-3546691
Email : lotuslab@streamyx.com Company No. : 437254-M
Specialised in analysis of Edible Oils and its products, Drinking Water and Waste Water, Foods, Animal Feeds, Chemicals, Fuel Oils, Environmental Monitoring, etc...

REPORT

OUR REF : **LS/B4334/08 (O1)**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : One (1) plastic bag containing sample was received and said to be Green Bentonite (GB)

Test Results :-

NAME	GBUT
Solution Analysis	**RESULT**
Phosphorus (as P)	0.5 ppm
Aluminium (as Al)	250.0 ppm
Silica (as SiO_2)	40.0 ppm
Calcium (as Ca)	0.04 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 1 month cured Green Bentonite

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REPORT

OUR REF	:	**LS/B4780/08**
DATE	:	**27th September, 2008**
COMPANY	:	**AMIN EISAZADEH**
DATE SAMPLE RECEIVED	:	**17th September, 2008** .
SAMPLE DESCRIPTION	:	Four (4) plastic bags containing samples were received and said to be Green Bentonie (GB)

Test Results :-

NAME	GBAT 1% 1M	GBAT 7% 1M	GBLT 3% 1M	GBLT 10% 1M
Solution Analysis	RESULTS			
Phosphorus (as P)	141.0 ppm	71.6 ppm	-	-
Aluminium (as Al)	513.9 ppm	5.7 ppm	173.8 ppm	0.1 ppm
Silica (as SiO_2)	42.5 ppm	0.3 ppm	500 ppm	100.0 ppm
Calcium (as Ca)	-	-	0.8 ppm	1.9 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 4 months cured Green Bentonite

LOTUS LABORATORY SERVICES (M) SDN. BHD.
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REPORT

OUR REF : **LS/B4334/08**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Green Bentonite (GB)

Test Results :-

NAME	GBAT 1% 4M	GBAT 7% 4M	GBLT 3% 4M	GBLT 10% 4M
Solution Analysis	RESULTS			
Phosphorus (as P)	146.0 ppm	187.0 ppm	-	-
Aluminium (as Al)	884.0 ppm	38.3 ppm	442 ppm	17.3 ppm
Silica (as SiO_2)	45.0 ppm	1.0 ppm	250.0 ppm	80.0 ppm
Calcium (as Ca)	-	-	0.8 ppm	0.7 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chamist
B. App. Sc.(Hons.).

Leaching test results for 8 months cured Green Bentonite

LOTUS LABORATORY SERVICES (M) SDN. BHD.
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REPORT

OUR REF : **LS/B4615/08**

DATE : **29th August, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **20th August, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Green Bentonite (GB)

Test Results :-

NAME	GBAT 1% 8M	GBAT 7% 8M	GBLT 3% 8M	GBLT 10% 8M
Solution Analysis	RESULTS			
Phosphorus (as P)	106.4 ppm	78.1 ppm	-	-
Aluminium (as Al)	539.5 ppm	15.7 ppm	300.0 ppm	0.9 ppm
Silica (as SiO_2)	20.0 ppm	0.5 ppm	250.0 ppm	80.0 ppm
Calcium (as Ca)	-	-	0.6 ppm	0.4 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
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Leaching test results for untreated Laterite Clay

LOTUS LABORATORY SERVICES (M) SDN. BHD.
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REPORT

OUR REF : **LS/B4333/08 (O1)**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : One (1) plastic bag containing sample was received and said to be Laterite Clay (LC)

Test Results :-

NAME	LCUT
Solution Analysis	**RESULT**
Phosphorus (as P)	0.4 ppm
Aluminium (as Al)	0.05 ppm
Silica (as SiO_2)	0.1 ppm
Calcium (as Ca)	0.1 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
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Leaching test results for 1 month cured Laterite Clay

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REPORT

OUR REF : **LS/B4778/08**

DATE : **27th September, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **17th September, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Laterite Clay (LC)

Test Results :-

NAME	LCAT 1% 1M	LCAT 7% 1M	LCLT 3% 1M	LCLT 7% 1M
Solution Analysis	RESULTS			
Phosphorus (as P)	8.9 ppm	66.2 ppm	-	-
Aluminium (as Al)	2.6 ppm	9.3 ppm	39.6 ppm	40.8 ppm
Silica (as SiO_2)	20.0 ppm	0.3 ppm	0.7 ppm	1.8 ppm
Calcium (as Ca)	-	-	192.4 ppm	214.5 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 4 months cured Laterite Clay

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REPORT

OUR REF : **LS/B4333/08**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Laterite Clay (LC)

Test Results :-

NAME	LCAT 1% 4M	LCAT 7% 4M	LCLT 3% 4M	LCLT 7% 4M
Solution Analysis	RESULTS			
Phosphorus (as P)	12.6 ppm	171.1 ppm	-	-
Aluminium (as Al)	3.9 ppm	30.7 ppm	30.8 ppm	33.9 ppm
Silica (as SiO_2)	27.0 ppm	1.5 ppm	0.7 ppm	1.5 ppm
Calcium (as Ca)	-	-	114.0 ppm	168.5 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 8 months cured Laterite Clay

LOTUS LABORATORY SERVICES (M) SDN. BHD.
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REPORT

OUR REF : **LS/B4617/08**

DATE : **30th August, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **20th August, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Laterite Clay (LC)

Test Results :-

NAME	LCAT 1% 8M	LCAT 7% 8M	LCLT 3% 8M	LCLT 7% 8M
Solution Analysis	RESULTS			
Phosphorus (as P)	4.0 ppm	68.4 ppm	-	-
Aluminium (as Al)	1.5 ppm	55.2 ppm	29.4 ppm	23.7 ppm
Silica (as SiO_2)	20.0 ppm	0.3 ppm	0.6 ppm	1.5 ppm
Calcium (as Ca)	-	-	41.5 ppm	78.2 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for untreated White Kaolin

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REPORT

OUR REF : **LS/B4331/08 (O1)**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : One (1) plastic bag containing sample was received and said to be White Kaolin (WK)

Test Results :-

NAME	WKUT
Solution Analysis	**RESULT**
Phosphorus (as P)	5.1 ppm
Aluminium (as Al)	5.8 ppm
Silica (as SiO_2)	4.0 ppm
Calcium (as Ca)	0.4 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
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Leaching test results for 1 month cured White Kaolin

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REPORT

OUR REF : **LS/B4777/08**

DATE : **27th September, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **17th September, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be White Kaolin (WK)

Test Results :-

NAME	WKAT 1% 1M	WKAT 5% 1M	WKLT 1% 1M	WKLT 5% 1M
Solution Analysis	RESULTS			
Phosphorus (as P)	65.4 ppm	67.5 ppm	-	-
Aluminium (as Al)	10.4 ppm	78.7 ppm	5.6 ppm	0.9 ppm
Silica (as SiO_2)	0.2 ppm	0.3 ppm	6.5 ppm	0.3 ppm
Calcium (as Ca)	-	-	178 ppm	295.5 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
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Leaching test results for 4 months cured White Kaolin

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REPORT

OUR REF : **LS/B4331/08**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be White Kaolin (WK)

Test Results :-

NAME	WKAT 1% 4M	WKAT 5% 4M	WKLT 1% 4M	WKLT 5% 4M
Solution Analysis	RESULTS			
Phosphorus (as P)	174.5 ppm	184.3 ppm	-	-
Aluminium (as Al)	20.9 ppm	182.7 ppm	6.8 ppm	7.1 ppm
Silica (as SiO_2)	0.5 ppm	0.7 ppm	3.3 ppm	1.3 ppm
Calcium (as Ca)	-	-	30.3 ppm	186.3 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 8 months cured White Kaolin

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REPORT

OUR REF : **LS/B4618/08**

DATE : **30th August, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **20th August, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be White Kaolin (WK)

Test Results :-

NAME	WKAT 1% 8M	WKAT 5% 8M	WKLT 1% 8M	WKLT 5% 8M
Solution Analysis	RESULTS			
Phosphorus (as P)	72.6 ppm	73.6 ppm	-	-
Aluminium (as Al)	20.0 ppm	172.5 ppm	15.2 ppm	18.3 ppm
Silica (as SiO_2)	0.2 ppm	0.3 ppm	2.5 ppm	4.0ppm
Calcium (as Ca)	-	-	18.3 ppm	52.7 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for untreated Pink Soil

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REPORT

OUR REF : **LS/B4332/08 (O1)**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : One (1) plastic bag containing samples was received and said to be Pink Soil (PS)

Test Results :-

NAME	PSUT
Solution Analysis	**RESULT**
Phosphorus (as P)	3.5 ppm
Aluminium (as Al)	0.6 ppm
Silica (as SiO_2)	4.0 ppm
Calcium (as Ca)	0.4 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 1 month cured Pink Soil

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REPORT

OUR REF : **LS/B4779/08**

DATE : **27th September, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **17th September, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Pink Soil (PS)

Test Results :-

NAME	PSAT 1% 1M	PSAT 5% 1M	PSLT 1% 1M	PSLT 5% 1M
Solution Analysis	RESULTS			
Phosphorus (as P)	60.2 ppm	66.9 ppm	-	-
Aluminium (as Al)	12.5 ppm	91.3 ppm	3.4 ppm	60.6 ppm
Silica (as SiO_2)	0.2 ppm	0.3 ppm	2.5 ppm	1.3 ppm
Calcium (as Ca)	-	-	85 ppm	86.6 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 4 months cured Pink Soil

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REPORT

OUR REF : **LS/B4332/08**

DATE : **26th July, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **15th July, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Pink Soil (PS)

Test Results :-

NAME	PSAT 1% 4M	PSAT 5% 4M	PSLT 1% 4M	PSLT 5% 4M
Solution Analysis	RESULTS			
Phosphorus (as P)	80.0 ppm	183.4 ppm	-	-
Aluminium (as Al)	13.3 ppm	76.1 ppm	3.6 ppm	13.2 ppm
Silica (as SiO_2)	1.8 ppm	0.8 ppm	2.3 ppm	3.5 ppm
Calcium (as Ca)	-	-	41.6 ppm	45.3 ppm

LOTUS LABORATORY SERVICES (M) SDN BHD

CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Leaching test results for 8 months cured Pink Soil

LOTUS LABORATORY SERVICES (M) SDN. BHD.
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Email : lotuslab@streamyx.com Company No. : 437254-M
Specialised in analysis of Edible Oils and its products, Drinking Water and Waste Water, Foods, Animal Feeds, Chemicals, Fuel Oils, Environmental Monitoring, etc...

REPORT

OUR REF : **LS/B4616/08**

DATE : **30th August, 2008**

COMPANY : **AMIN EISAZADEH**

DATE SAMPLE RECEIVED : **20th August, 2008**

SAMPLE DESCRIPTION : Four (4) plastic bags containing samples were received and said to be Pink Soil (PS)

Test Results :-

NAME	PSAT 1% 8M	PSAT 5% 8M	PSLT 1% 8M	PSLT 5% 8M
Solution Analysis	RESULTS			
Phosphorus (as P)	58.6 ppm	73.7 ppm	-	-
Aluminium (as Al)	10.2 ppm	71.6 ppm	16.7 ppm	24.4 ppm
Silica (as SiO_2)	0.4 ppm	0.3 ppm	2.3 ppm	1.8 ppm
Calcium (as Ca)	-	-	19.5 ppm	28.1 ppm

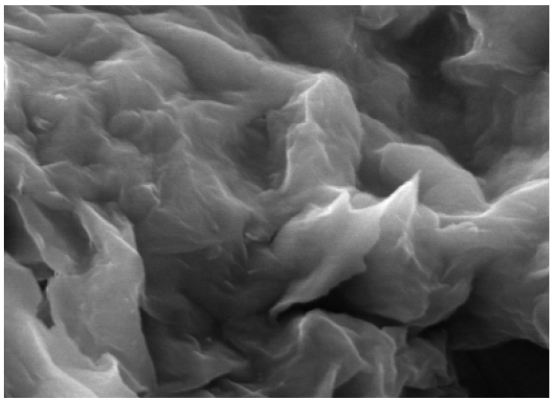
LOTUS LABORATORY SERVICES (M) SDN BHD

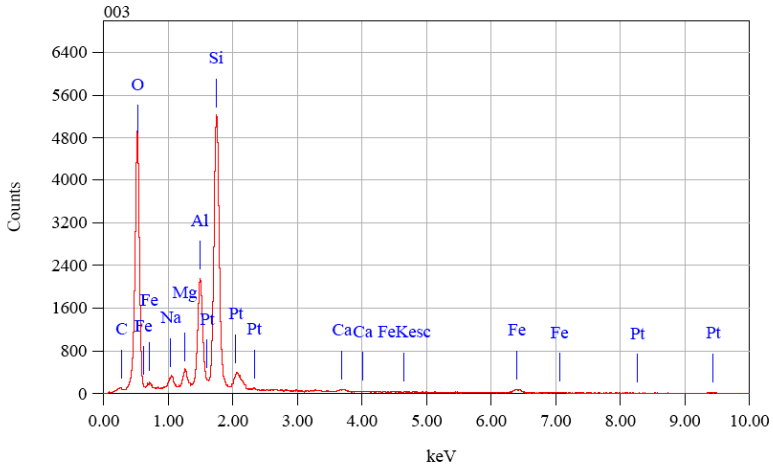
CHIN SYEK YUN, Quality Manager/Chemist
B. App. Sc.(Hons.), AMIC

Appendix B

EDAX analysis of untreated Green Bentonite

```
Title        : GBUT
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/02/15
Pixel        : 512 x 384
```





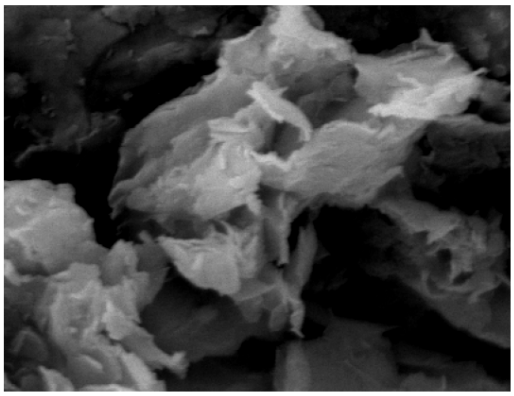

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 71.52 sec
Live Time     : 50.00 sec
Dead Time     : 30 %
Counting Rate: 3544 cps
Energy Range :  0 - 20 keV
```

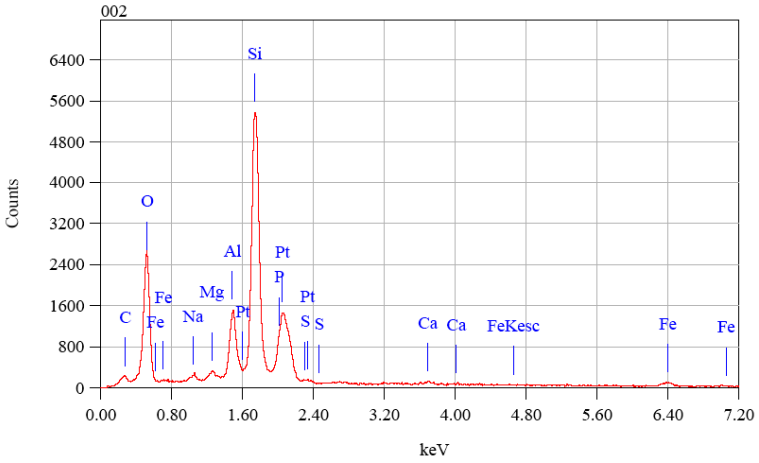
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1481

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	2.03	0.14	3.60				0.3402
O K	0.525	47.64	0.10	63.33				60.1759
Na K	1.041	1.39	0.11	1.29				1.2446
Mg K	1.253	1.58	0.09	1.38				1.3065
Al K	1.486	9.56	0.09	7.53				8.9915
Si K	1.739	27.55	0.10	20.86				27.2578
Ca K	3.690	0.39	0.21	0.21				0.4855
Fe K	6.398	2.69	0.57	1.02				2.9051
Pt M	2.048	7.17	0.46	0.78				4.8916
Total		100.00		100.00				

EDAX analysis of acid treated Green Bentonite

```
Title        : GBAT7%8M
-----------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/08/27
Pixel        : 512 x 384
```





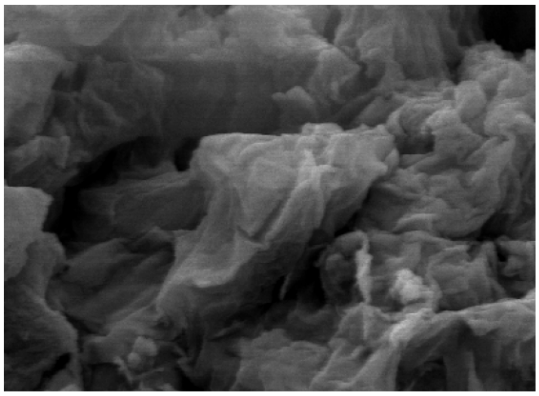

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 76.29 sec
Live Time     : 50.00 sec
Dead Time     : 35 %
Counting Rate: 4287 cps
Energy Range :  0 - 20 keV
```

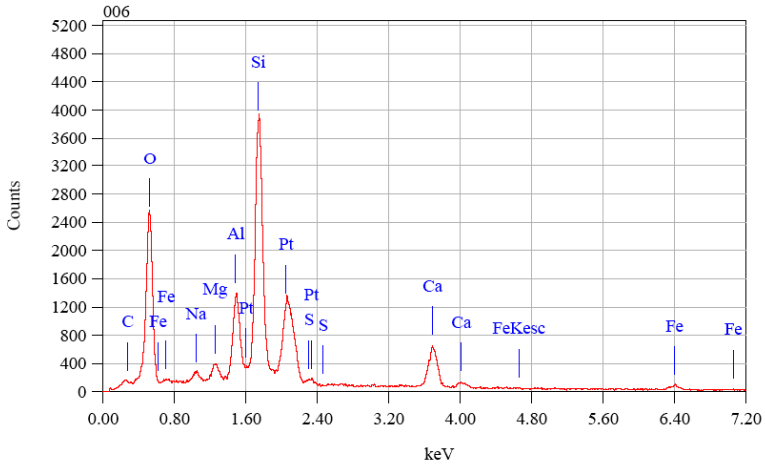
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1741

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	4.73	0.11	10.47				0.9328
O K	0.525	30.06	0.10	49.93				33.9347
Na K	1.041	0.72	0.08	0.83				0.7832
Mg K	1.253	0.66	0.07	0.72				0.6581
Al K	1.486	5.66	0.07	5.57				6.4646
Si K	1.739	24.73	0.07	23.40				30.8597
P K	2.013	4.06	0.09	3.48				4.7579
S K	2.307	0.54	0.09	0.45				0.5796
Ca K	3.690	0.56	0.16	0.37				0.7928
Fe K	6.398	2.71	0.42	1.29				3.5646
Pt M	2.048	25.60	0.34	3.49				22.3189
Total		100.00		100.00				

EDAX analysis of lime treated Green Bentonite

```
Title        : GBLT10%8M
---------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/08/27
Pixel        : 512 x 384
```





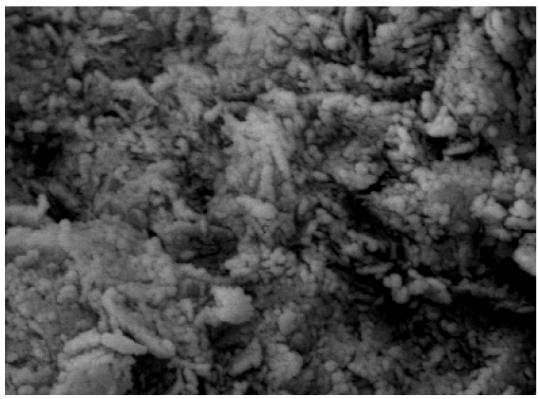

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 72.56 sec
Live Time     : 50.00 sec
Dead Time     : 30 %
Counting Rate: 3607 cps
Energy Range :  0 - 20 keV
```

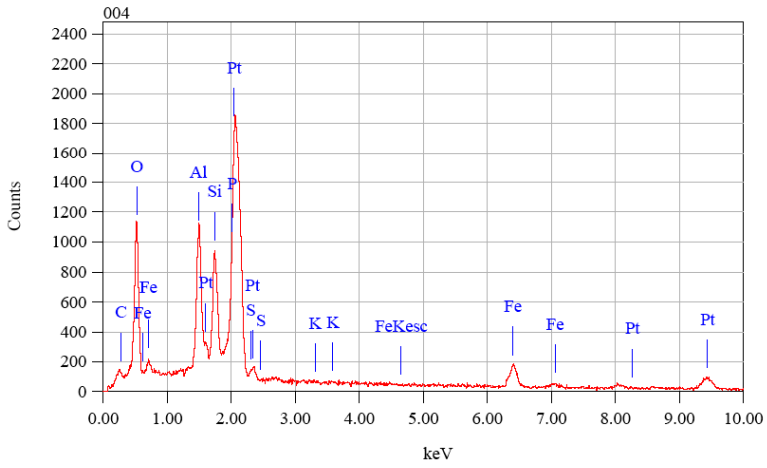
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1790

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	1.65	0.09	3.68				0.3893
O K	0.525	35.01	0.11	58.53				36.7034
Na K	1.041	0.94	0.08	1.10				0.9622
Mg K	1.253	1.25	0.07	1.38				1.1829
Al K	1.486	5.97	0.07	5.92				6.4580
Si K	1.739	20.08	0.08	19.12				23.9418
S K	2.307	0.88	0.09	0.74				0.9789
Ca K	3.690	7.47	0.16	4.99				10.6080
Fe K	6.398	2.60	0.42	1.25				3.3638
Pt M	2.048	24.15	0.32	3.31				21.0783
Total		100.00		100.00				

EDAX analysis of untreated Laterite Clay

```
Title        : LCUT
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/02/18
Pixel        : 512 x 384
```





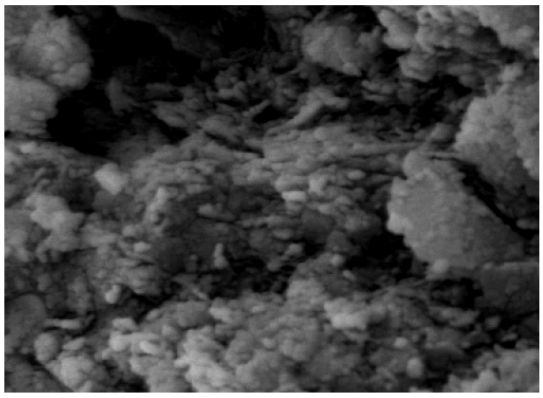

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 64.98 sec
Live Time     : 50.00 sec
Dead Time     : 23 %
Counting Rate: 2559 cps
Energy Range :  0 - 20 keV
```

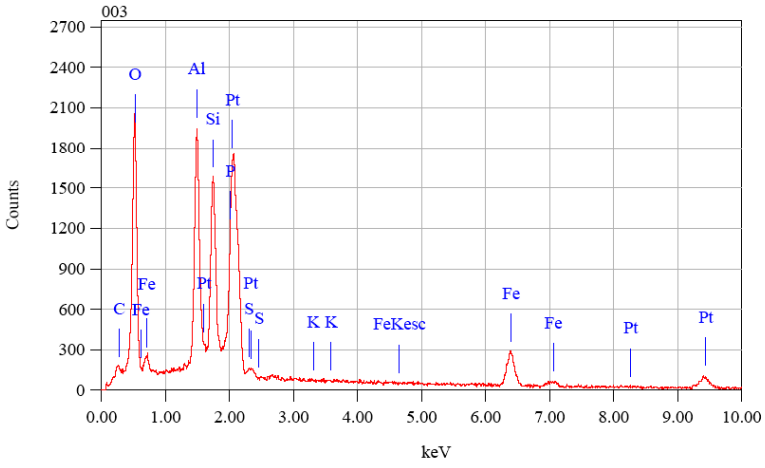
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2356

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	1.78	0.06	5.95				0.4766
O K	0.525	20.67	0.08	51.69				22.3677
Al K	1.486	6.79	0.05	10.07				7.2093
Si K	1.739	6.02	0.06	8.58				7.0985
P K	2.013	4.28	0.06	5.53				5.6277
S K	2.307	1.18	0.07	1.48				1.2016
K K	3.312	0.19	0.11	0.19				0.2265
Fe K	6.398	8.60	0.30	6.16				11.6366
Pt M	2.048	50.49	0.23	10.36				49.1462
Total		100.00		100.00				

EDAX analysis of acid treated Laterite Clay

```
Title        : LCAT7%8M
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/08/29
Pixel        : 512 x 384
```





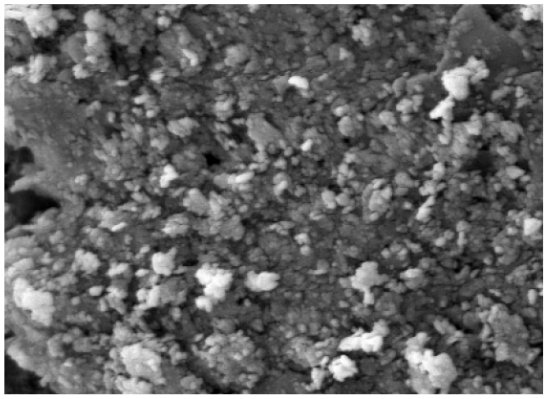

```
Acquisition Parameter
Instrument   : 6701F
Acc. Voltage : 15.0 kV
Probe Current: 2.56160 nA
PHA mode     : T4
Real Time    : 69.28 sec
Live Time    : 50.00 sec
Dead Time    : 27 %
Counting Rate: 3181 cps
Energy Range :  0 - 20 keV
```

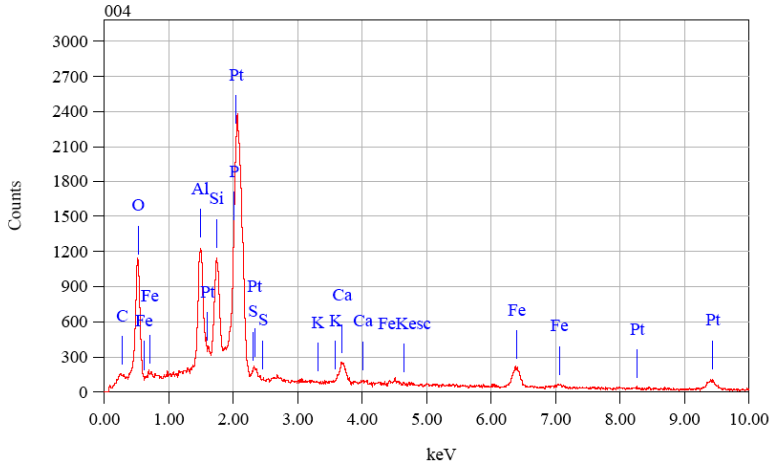
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2197

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	2.20	0.08	5.95				0.5181
O K	0.525	26.38	0.09	53.51				30.3367
Al K	1.486	9.60	0.06	11.55				9.9692
Si K	1.739	8.57	0.07	9.90				9.6232
P K	2.013	5.51	0.08	5.77				6.7898
S K	2.307	0.86	0.08	0.87				0.8894
K K	3.312	0.00	0.12	0.00				0.0033
Fe K	6.398	11.21	0.36	6.52				14.6585
Pt M	2.048	35.66	0.28	5.93				32.5897
Total		100.00		100.00				

EDAX analysis of lime treated Laterite Clay

```
Title        : LCLT7%8M
---------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 5,000
Date         : 2008/08/29
Pixel        : 512 x 384
```





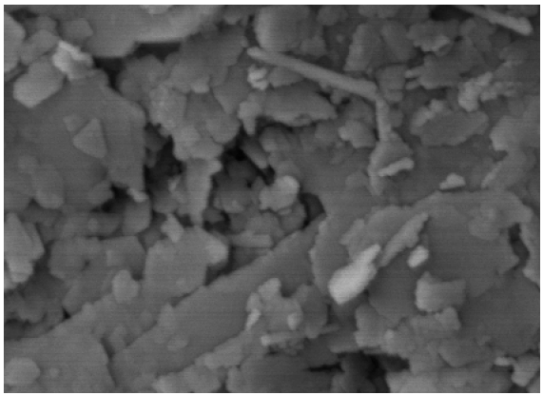

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 69.72 sec
Live Time     : 50.00 sec
Dead Time     : 27 %
Counting Rate: 3166 cps
Energy Range :  0 - 20 keV
```

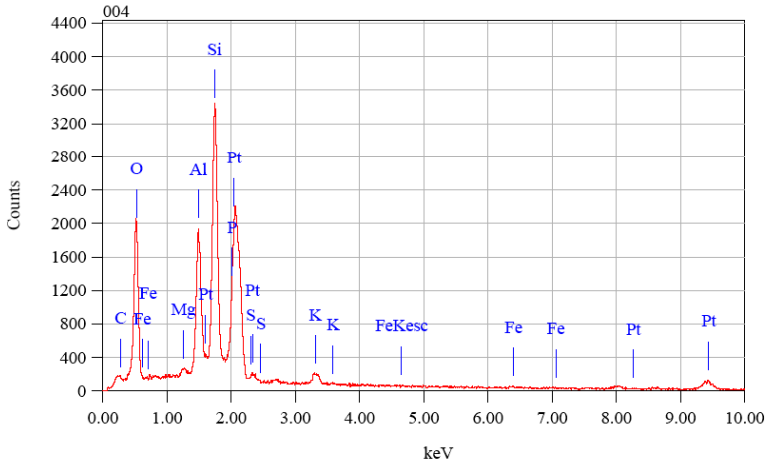
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2456

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	1.28	0.06	4.55				0.3407
O K	0.525	17.97	0.09	47.83				18.1567
Al K	1.486	6.10	0.06	9.64				6.4525
Si K	1.739	5.77	0.06	8.75				6.8035
P K	2.013	5.24	0.07	7.21				6.8903
S K	2.307	1.32	0.08	1.75				1.3231
K K								
Ca K	3.690	2.62	0.13	2.79				3.5431
Fe K	6.398	8.18	0.32	6.24				10.9859
Pt M	2.048	51.51	0.24	11.24				50.1372
Total		100.00		100.00				

EDAX analysis of untreated White Kaolin

```
Title        : WKUT
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/02/25
Pixel        : 512 x 384
```





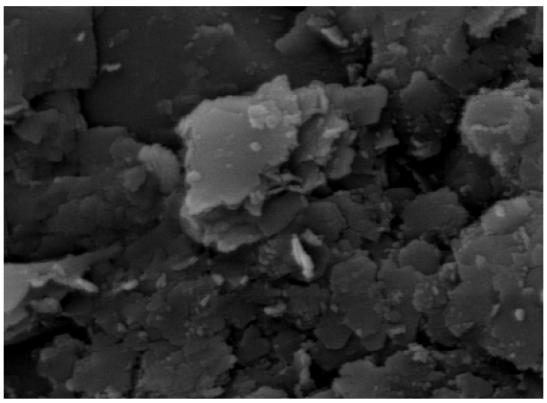

```
Acquisition Parameter
Instrument   : 6701F
Acc. Voltage : 15.0 kV
Probe Current: 2.56160 nA
PHA mode     : T4
Real Time    : 74.01 sec
Live Time    : 50.00 sec
Dead Time    : 32 %
Counting Rate: 3820 cps
Energy Range :  0 - 20 keV
```

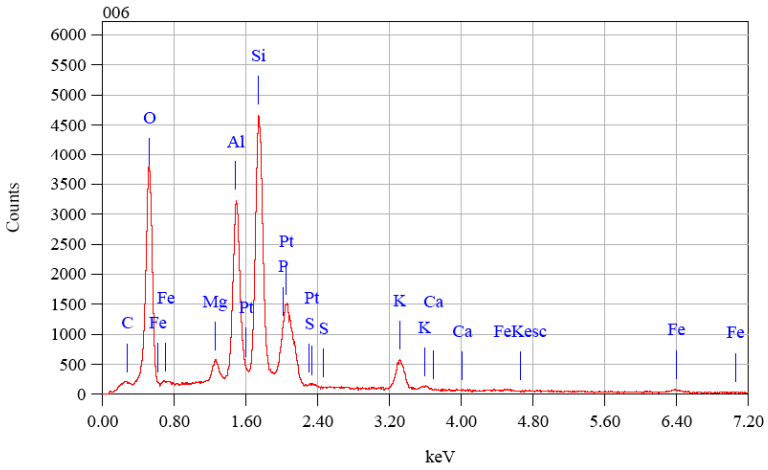
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1825

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	0.84	0.07	2.34				0.1922
O K	0.525	26.25	0.08	54.71				28.4421
Mg K	1.253	0.44	0.05	0.60				0.4452
Al K	1.486	7.68	0.05	9.50				8.8397
Si K	1.739	15.97	0.06	18.96				19.7912
P K	2.013	3.98	0.07	4.28				5.0260
S K	2.307	0.88	0.07	0.92				0.9130
K K	3.312	1.51	0.11	1.28				1.8886
Fe K	6.398	0.36	0.31	0.22				0.4913
Pt M	2.048	42.08	0.24	7.19				39.4502
Total		100.00		100.00				

EDAX analysis of acid treated White Kaolin

```
Title        : WKAT5%8M
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/08/28
Pixel        : 512 x 384
```





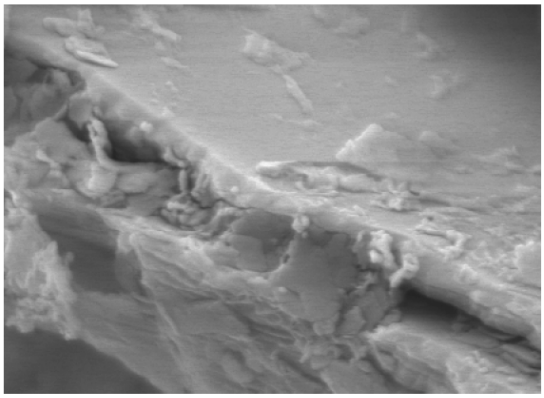

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 79.73 sec
Live Time     : 50.00 sec
Dead Time     : 37 %
Counting Rate: 4529 cps
Energy Range  :  0 - 20 keV
```

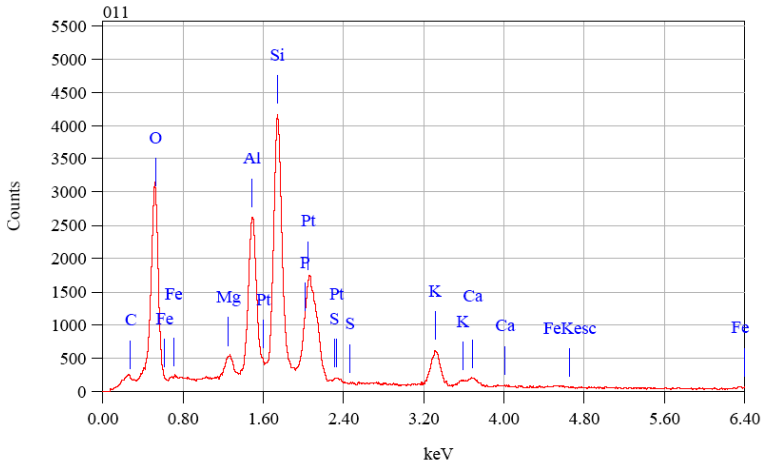
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1371

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	1.63	0.09	3.42				0.3264
O K	0.525	36.99	0.09	58.12				41.8476
Mg K	1.253	1.37	0.06	1.41				1.3332
Al K	1.486	11.18	0.06	10.42				12.2745
Si K	1.739	18.89	0.07	16.91				21.4837
P K	2.013	4.28	0.08	3.48				4.8563
S K	2.307	0.42	0.08	0.33				0.4500
K K	3.312	4.40	0.12	2.83				5.5921
Ca K								
Fe K	6.398	1.25	0.37	0.56				1.5646
Pt M	2.048	19.59	0.30	2.52				16.5029
Total		100.00		100.00				

EDAX analysis of lime treated White Kaolin

```
Title        : WKLT5%8M
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/08/28
Pixel        : 512 x 384
```





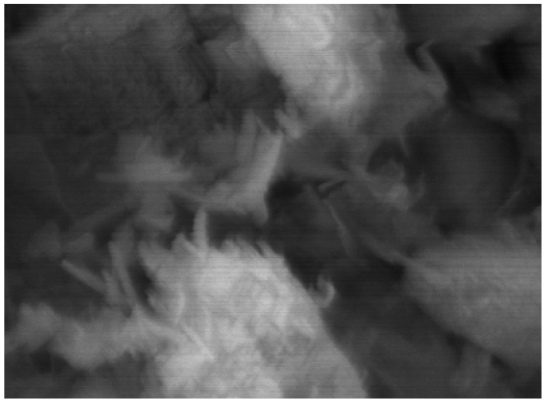

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 79.98 sec
Live Time     : 50.00 sec
Dead Time     : 36 %
Counting Rate: 4476 cps
Energy Range :  0 - 20 keV
```

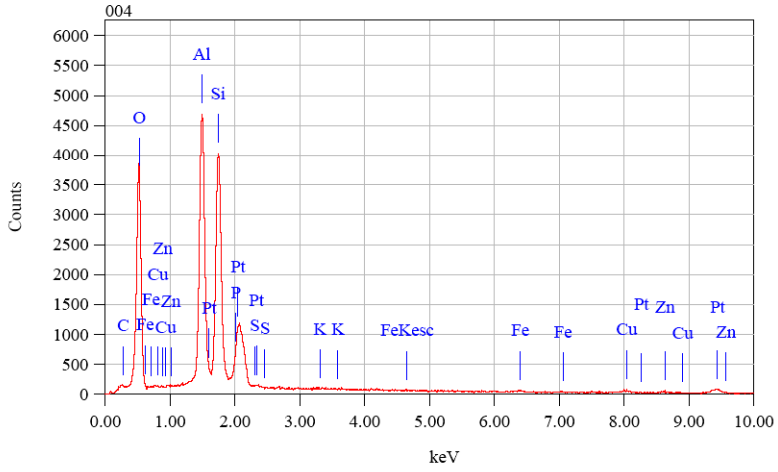
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1593

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	1.83	0.08	4.20				0.4139
O K	0.525	32.86	0.10	56.44				35.3229
Mg K	1.253	1.34	0.06	1.52				1.3423
Al K	1.486	9.27	0.06	9.44				10.4486
Si K	1.739	16.80	0.07	16.44				20.0827
P K	2.013	3.40	0.08	3.02				4.1192
S K	2.307	0.58	0.08	0.49				0.6304
K K	3.312	4.91	0.12	3.45				6.3720
Ca K	3.690	1.10	0.15	0.75				1.5324
Fe K	6.398	0.93	0.37	0.46				1.2150
Pt M	2.048	26.99	0.29	3.80				24.2815
Total		100.00		100.00				

EDAX analysis of untreated Pink Soil

```
Title        : PSUT
---------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/05/04
Pixel        : 512 x 384
```



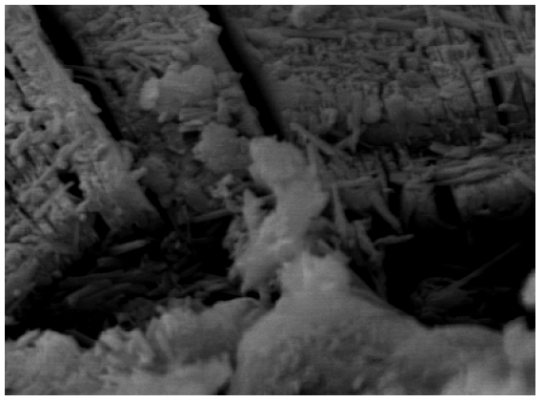



```
Acquisition Parameter
Instrument   : 6701F
Acc. Voltage : 15.0 kV
Probe Current: 2.56160 nA
PHA mode     : T4
Real Time    : 79.07 sec
Live Time    : 50.00 sec
Dead Time    : 35 %
Counting Rate: 4326 cps
Energy Range :  0 - 20 keV
```

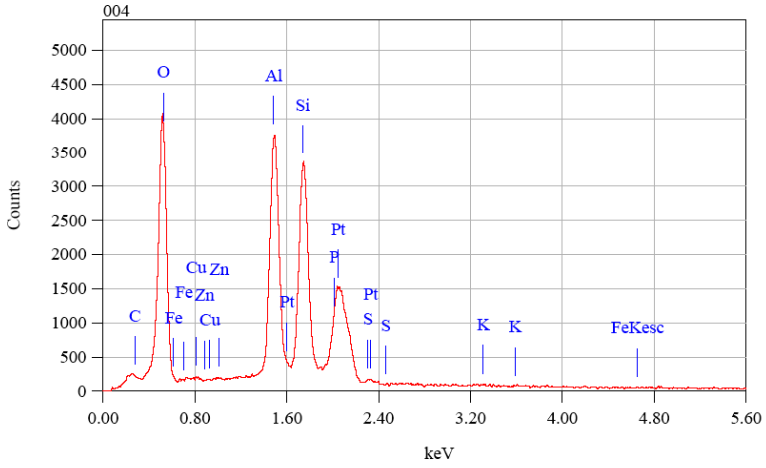
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1412

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	1.76	0.10	3.78				0.3313
O K	0.525	34.63	0.09	55.67				42.4996
Al K	1.486	17.96	0.06	17.12				19.2963
Si K	1.739	18.15	0.08	16.62				19.0845
P K	2.013	2.22	0.09	1.84				2.3952
S K	2.307	0.30	0.09	0.24				0.3124
K K	3.312	0.03	0.13	0.02				0.0345
Fe K	6.398	0.65	0.39	0.30				0.8170
Cu K	8.040	2.24	0.97	0.91				2.7185
Zn K	8.630	2.29	1.37	0.90				2.7678
Pt M	2.048	19.78	0.33	2.61				15.8945
Total		100.00		100.00				

EDAX analysis of acid treated Pink Soil



```
Title        : PSAT5%8M
-------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 10,000
Date         : 2008/08/29
Pixel        : 512 x 384
```



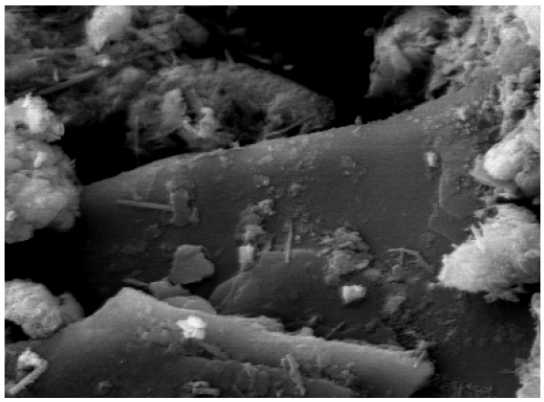

```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 76.82 sec
Live Time     : 50.00 sec
Dead Time     : 35 %
Counting Rate: 4223 cps
Energy Range :  0 - 20 keV
```

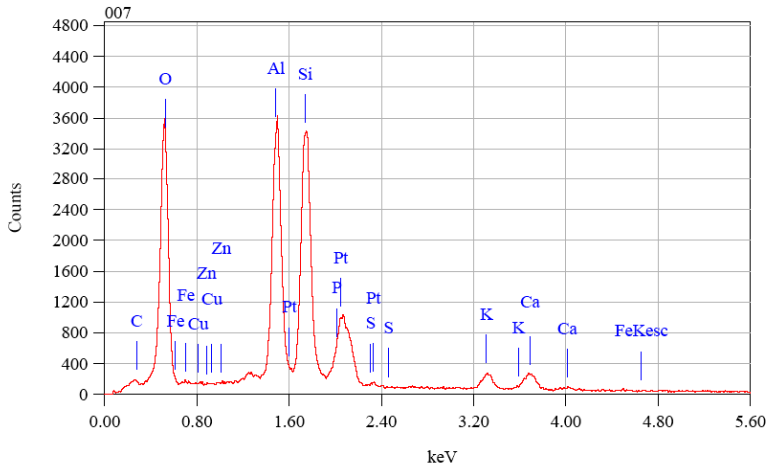
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1549

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	2.26	0.10	4.78				0.4572
O K	0.525	38.16	0.09	60.50				46.3993
Al K	1.486	14.35	0.07	13.49				15.5629
Si K	1.739	14.66	0.08	13.24				16.0598
P K	2.013	4.33	0.09	3.55				4.9477
S K	2.307	0.53	0.09	0.42				0.5581
K K	3.312	0.07	0.14	0.05				0.0900
Fe K	6.398	0.26	0.41	0.12				0.3298
Cu K	8.040	1.07	1.01	0.43				1.3045
Zn K	8.630	1.09	1.43	0.42				1.3244
Pt M	2.048	23.21	0.33	3.02				19.6991
Total		100.00		100.00				

EDAX analysis of lime treated Pink Soil

```
Title        : PSLT5%8M
---------------------------
Instrument   : 6701F
Volt         : 15.00 kV
Mag.         : x 5,000
Date         : 2008/08/29
Pixel        : 512 x 384
```






```
Acquisition Parameter
Instrument    : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56160 nA
PHA mode      : T4
Real Time     : 74.16 sec
Live Time     : 50.00 sec
Dead Time     : 32 %
Counting Rate: 3886 cps
Energy Range :  0 - 20 keV
```

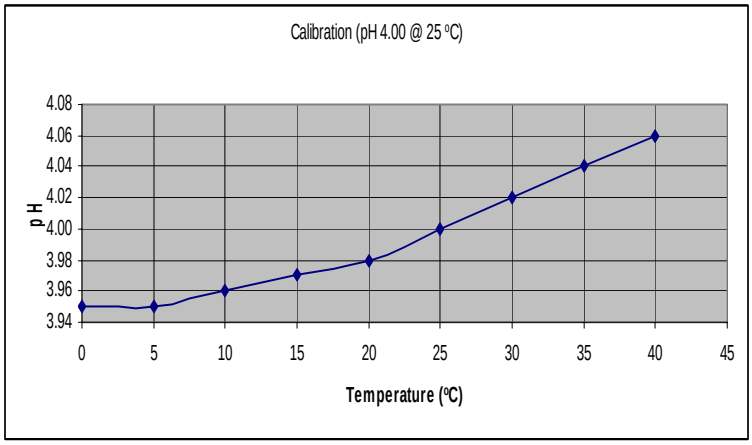
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1442

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	2.32	0.10	4.72				0.4882
O K	0.525	38.93	0.10	59.39				44.7289
Al K	1.486	14.78	0.07	13.37				16.2605
Si K	1.739	16.99	0.08	14.76				18.6920
P K	2.013	2.08	0.10	1.64				2.3329
S K	2.307	0.48	0.09	0.37				0.5271
K K	3.312	2.10	0.14	1.31				2.6961
Ca K	3.690	2.27	0.16	1.38				3.1418
Fe K	6.398	1.24	0.44	0.54				1.5523
Cu K	8.040	0.54	1.08	0.21				0.6499
Zn K	8.630	0.12	1.53	0.05				0.1493
Pt M	2.048	18.15	0.35	2.27				15.1692
Total		100.00		100.00				

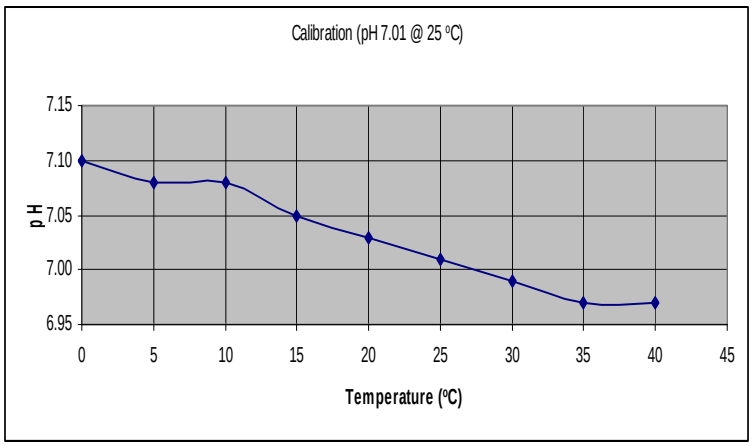
Appendix C

Calibration of pH meter

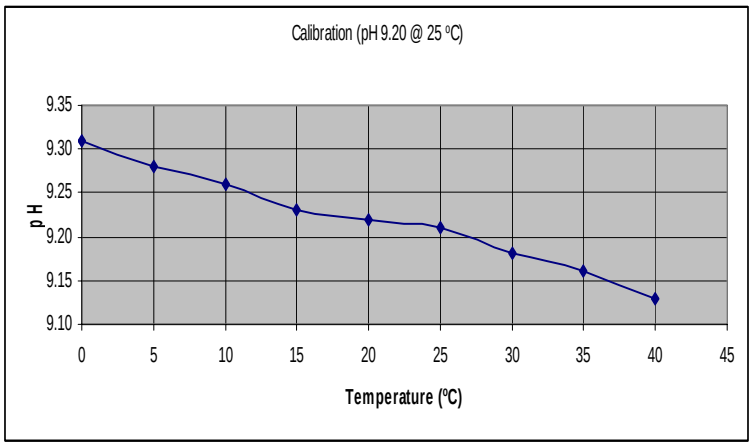
Temperature (^{o}C)	pH
0	3.95
5	3.95
10	3.96
15	3.97
20	3.98
25	4.00
30	4.02
35	4.04
40	4.06



Temperature (^{o}C)	pH
0	7.10
5	7.08
10	7.08
15	7.05
20	7.03
25	7.01
30	6.99
35	6.97
40	6.97



Temperature (^{o}C)	pH
0	9.31
5	9.28
10	9.26
15	9.23
20	9.22
25	9.21
30	9.18
35	9.16
40	9.13



Appendix D

Calibration of ICP for Ba analysis

Quantitative Analysis - Summary Report

Sample ID: Standard 1
Sample Date/Time: Thursday, June 12, 2008 21:03:16
Sample Description:
Solution Type: Standard
Blank File:
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Current Dead Time (ns): 35
Acq. Dead Time(ns): 35
Cumulative Autodilution Factor: 1

Sample File: C:\elandata\Sample\Ba FKA.sam
Method File: c:\elandata\Method\ba-fka.mth
Dataset File: c:\elandata\Dataset\totalquant analysis\Standard 1.1295
Tuning File: c:\elandata\Tuning\default.tun
Optimization File: c:\elandata\Optimize\default.dac
Calibration File: c:\elandata\System\New std 3.cal
Calibration Type: External Calibration

Summary

Concentration Results

Analyte	Mass	Conc. Mean	Sample Unit
Ba	138		mg/L

Quantitative Analysis - Summary Report

Sample ID: Standard 2
Sample Date/Time: Thursday, June 12, 2008 21:05:05
Sample Description:
Solution Type: Standard
Blank File:
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Current Dead Time (ns): 35
Acq. Dead Time(ns): 35
Cumulative Autodilution Factor: 1

Sample File: C:\elandata\Sample\Ba FKA.sam
Method File: c:\elandata\Method\ba-fka.mth
Dataset File: c:\elandata\Dataset\totalquant analysis\Standard 2.1296
Tuning File: c:\elandata\Tuning\default.tun
Optimization File: c:\elandata\Optimize\default.dac
Calibration File: c:\elandata\System\New std 3.cal
Calibration Type: External Calibration

Summary

Concentration Results

Analyte	Mass	Conc. Mean	Sample Unit
Ba	138	0.0208	mg/L

Quantitative Analysis - Summary Report

Sample ID: Standard 3
Sample Date/Time: Thursday, June 12, 2008 21:06:55
Sample Description:
Solution Type: Standard
Blank File:
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Current Dead Time (ns): 35
Acq. Dead Time(ns): 35
Cumulative Autodilution Factor: 1

Sample File: C:\elandata\Sample\Ba FKA.sam
Method File: c:\elandata\Method\ba-fka.mth
Dataset File: c:\elandata\Dataset\totalquant analysis\Standard 3.1297
Tuning File: c:\elandata\Tuning\default.tun
Optimization File: c:\elandata\Optimize\default.dac
Calibration File: c:\elandata\System\New std 3.cal
Calibration Type: External Calibration

Summary

Concentration Results

Analyte	Mass	Conc. Mean	Sample Unit
Ba	138	0.0440	mg/L

Quantitative Analysis - Summary Report

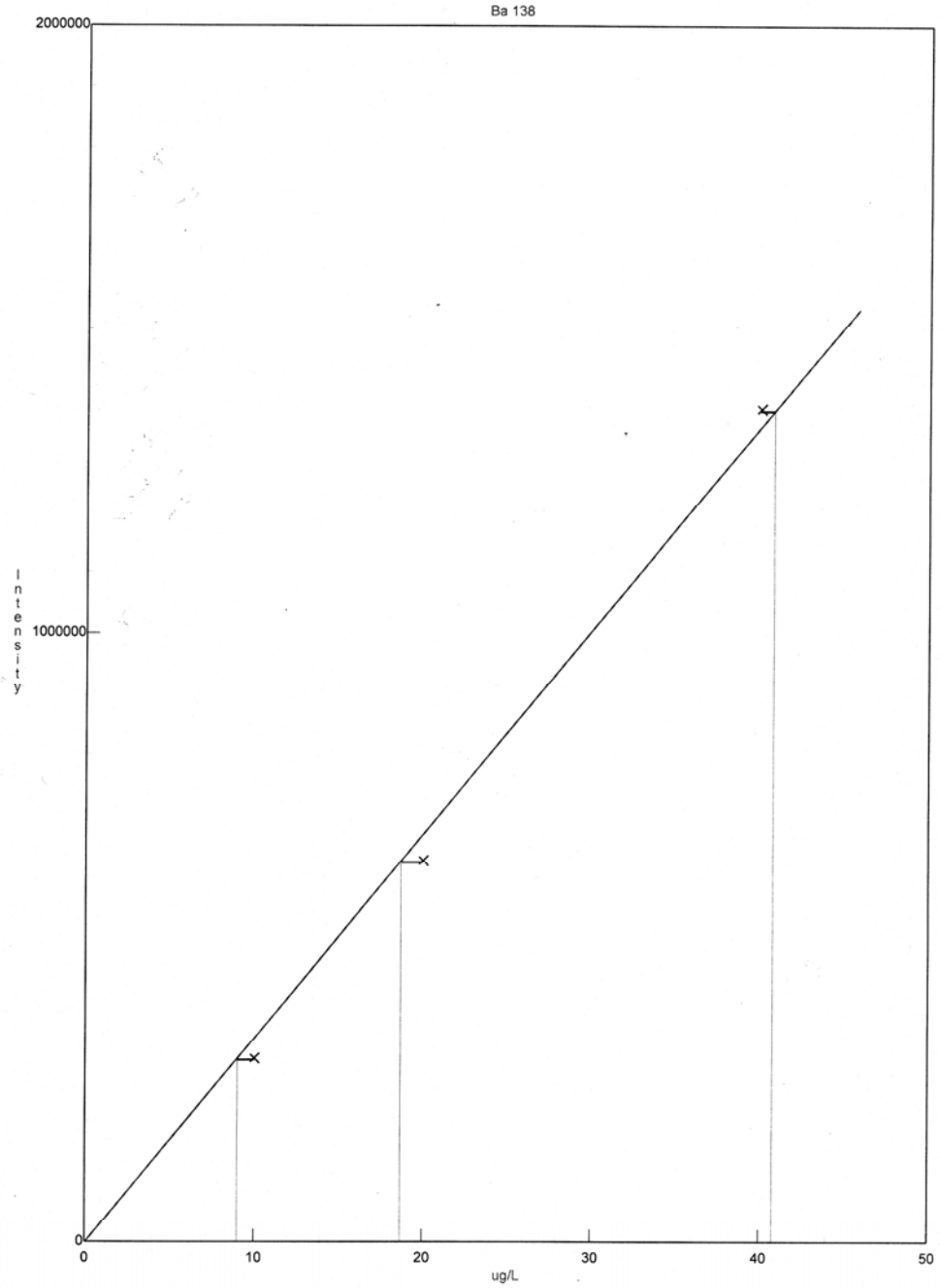
Sample ID: Ultra Pure Water
Sample Date/Time: Thursday, June 12, 2008 21:08:46
Sample Description: MR AMIN FKA
Solution Type: Sample
Blank File:
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Current Dead Time (ns): 35
Acq. Dead Time(ns): 35
Cumulative Autodilution Factor: 1

Sample File: C:\elandata\Sample\Ba FKA.sam
Method File: c:\elandata\Method\ba-fka.mth
Dataset File: c:\elandata\Dataset\totalquant analysis\Ultra Pure Water.1298
Tuning File: c:\elandata\Tuning\default.tun
Optimization File: c:\elandata\Optimize\default.dac
Calibration File: c:\elandata\System\New std 3.cal
Calibration Type: External Calibration

Summary

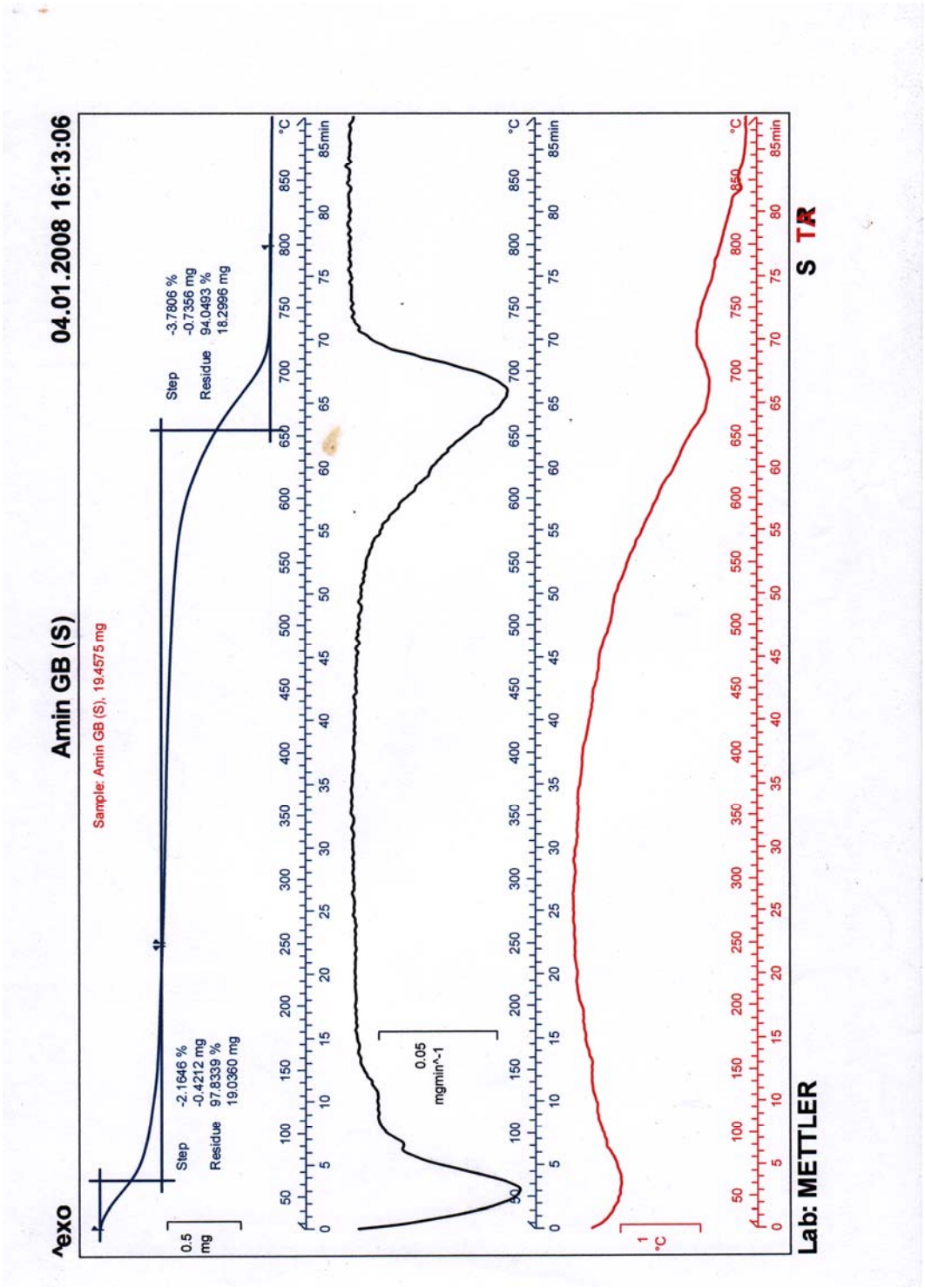
Concentration Results

Analyte	Mass	Conc. Mean	Sample Unit
Ba	138	0.0000	mg/L

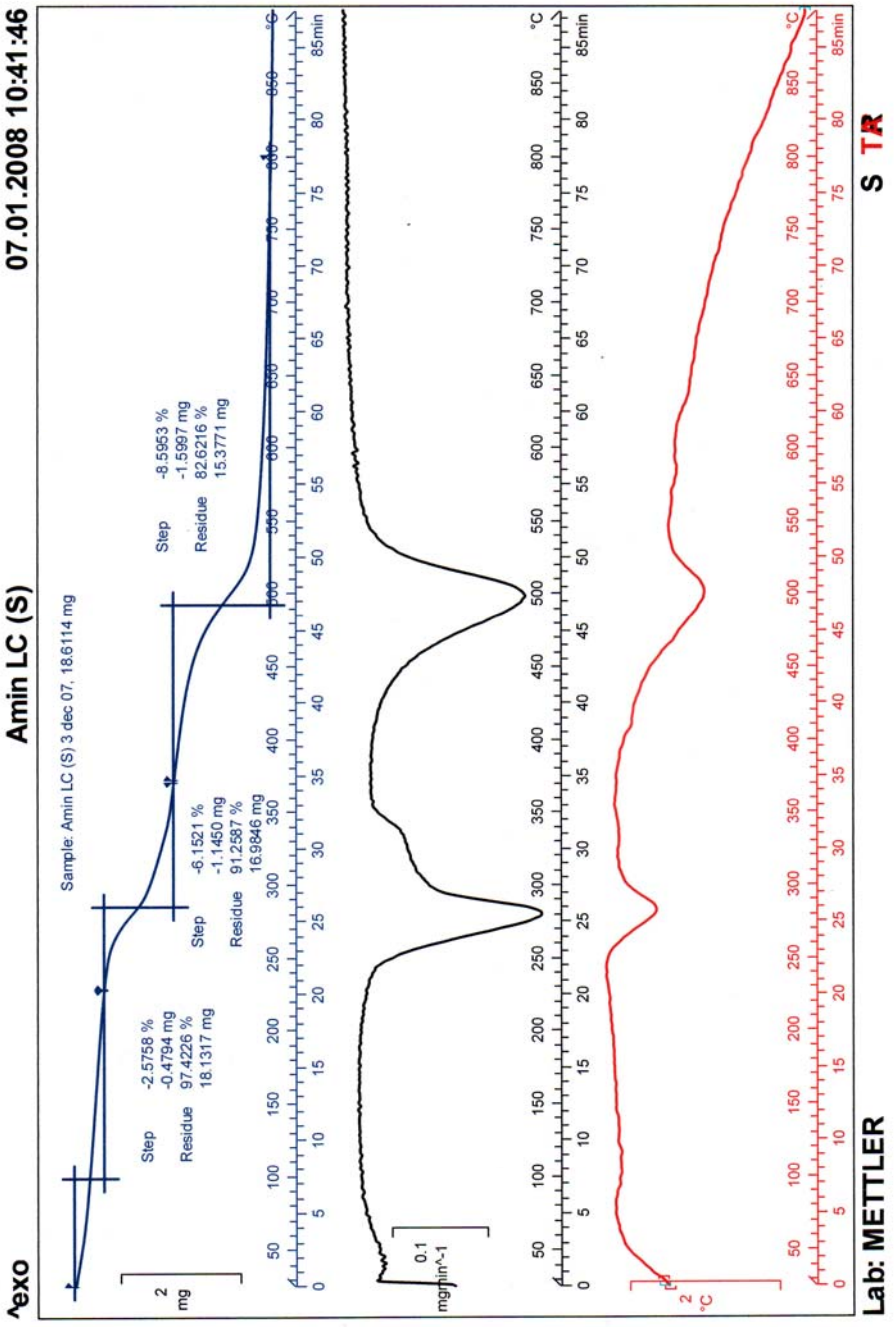

Ba 138
2000000
1000000
0
Intensity
0
10
20
30
40
50
ug/L

Appendix E

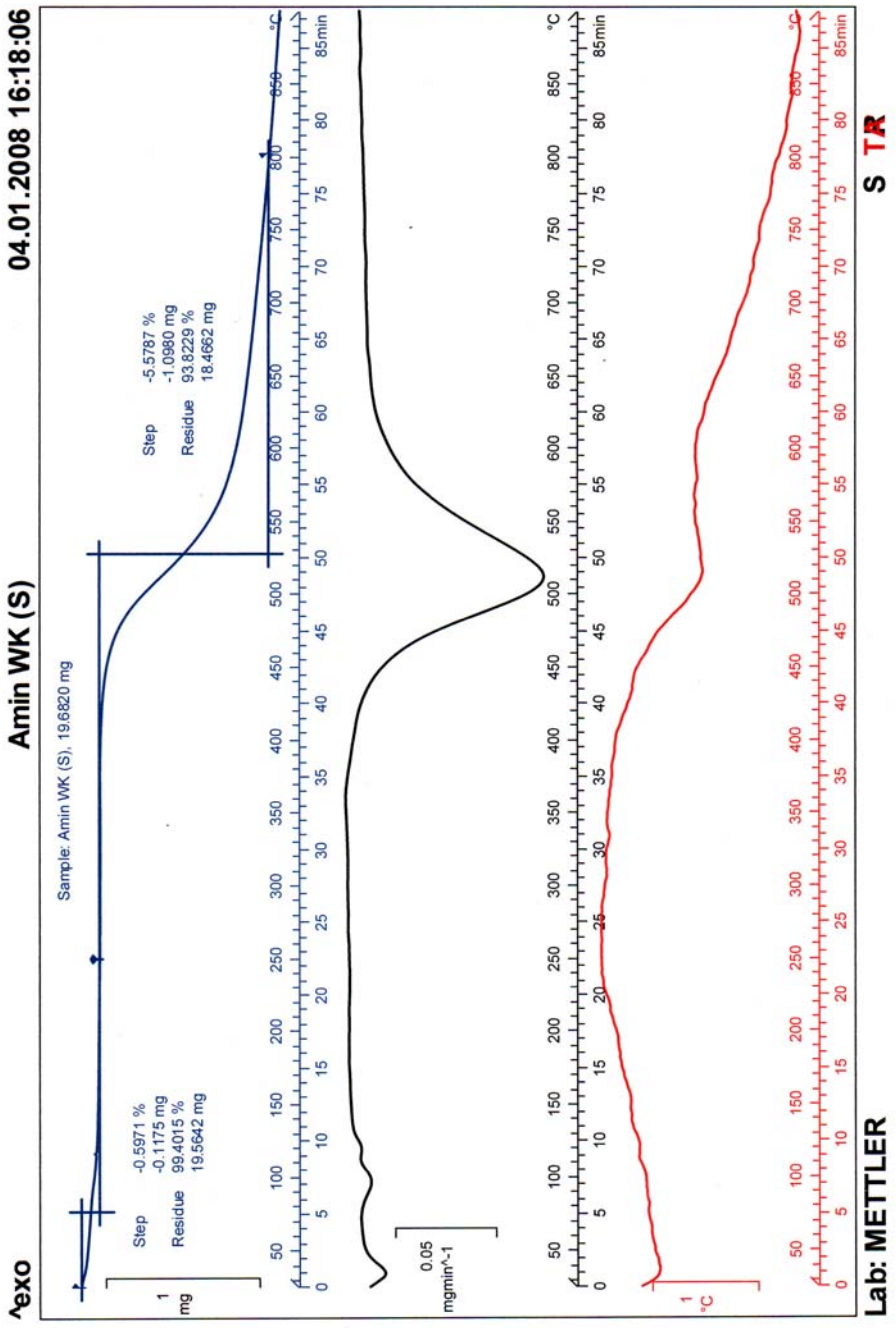
TGA analysis for untreated Green Bentonite



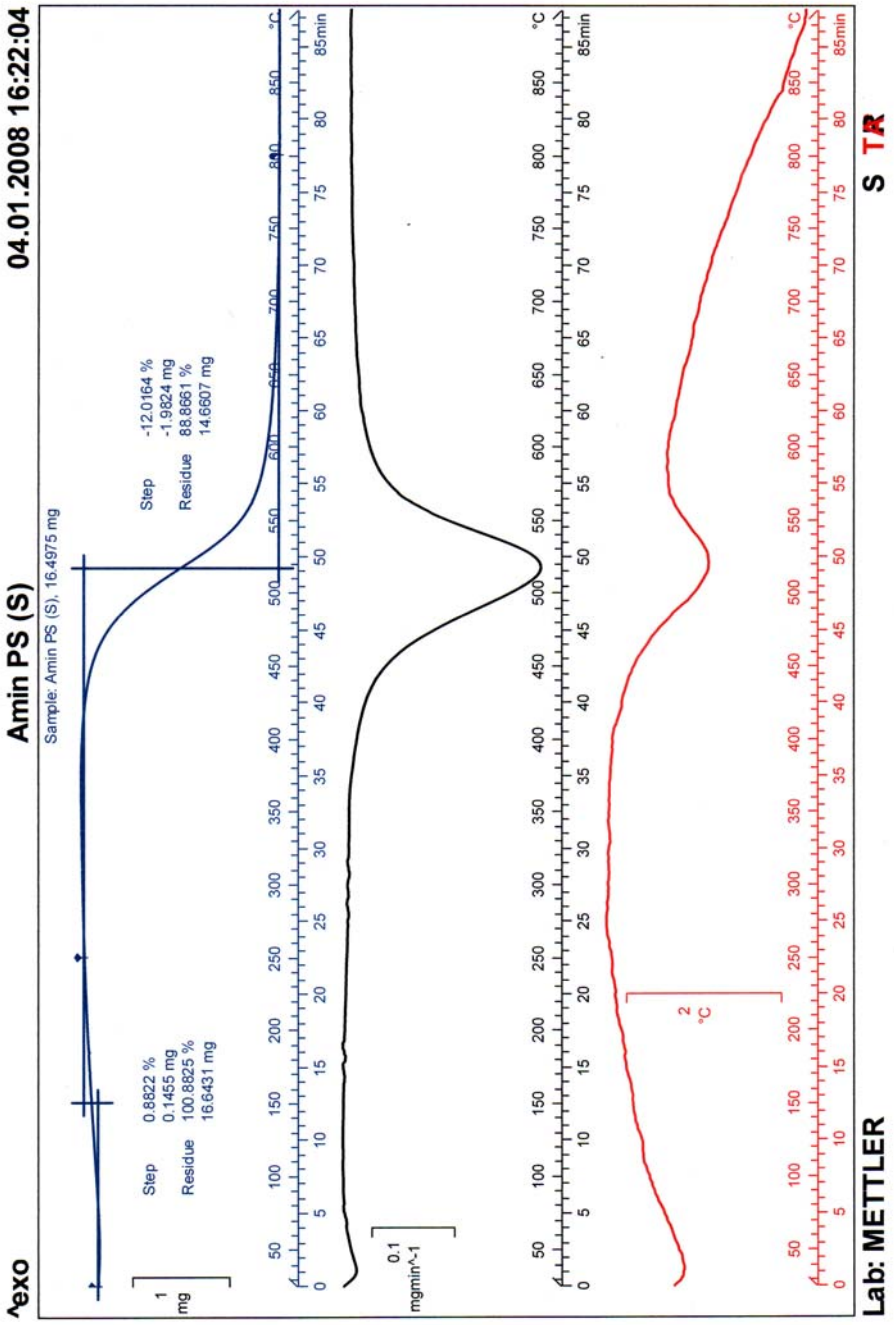
TGA analysis for untreated Laterite Clay



TGA analysis for untreated White Kaolin



TGA analysis for untreated Pink Soil



Appendix F

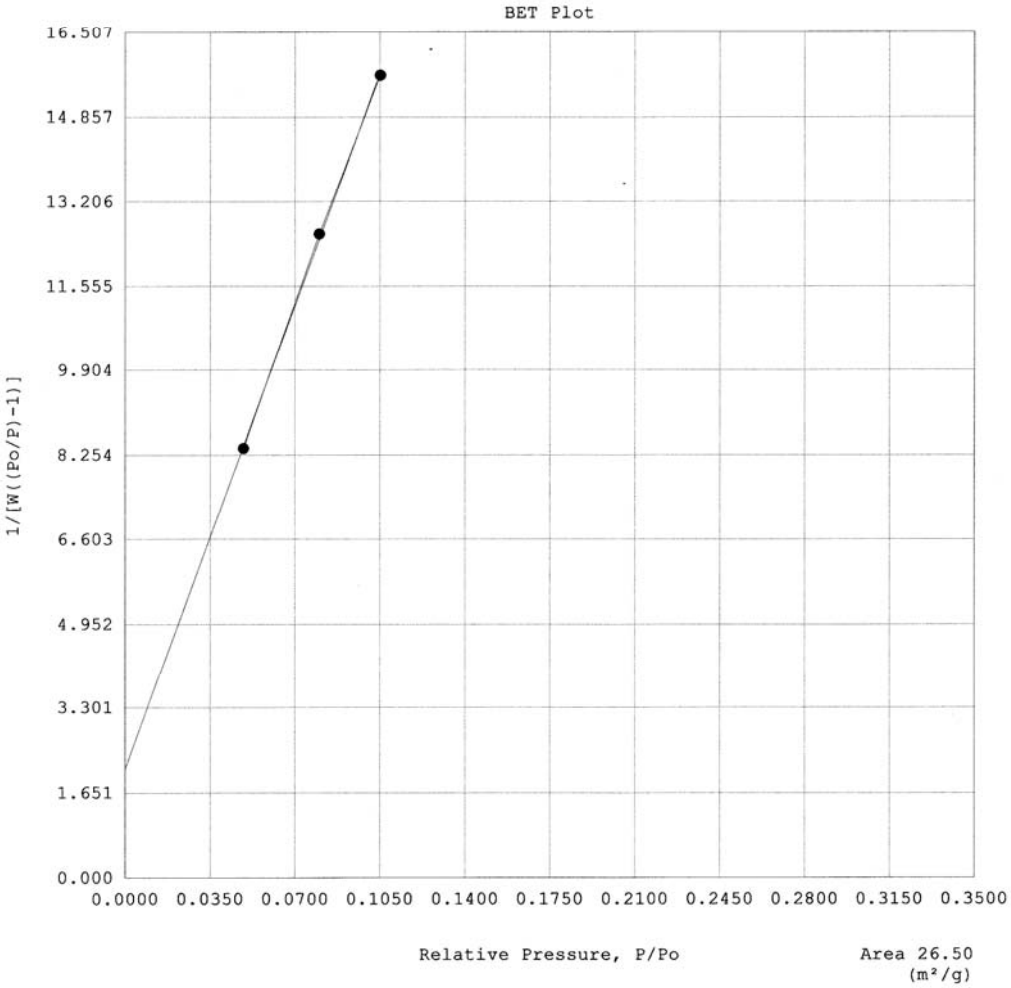
BET analysis of untreated Green Bentonite

06/23/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS862301GBUT 0% 4M.raw				
Sample ID:	GBUT 0% 4M	**Description:**	GBUT 0% 4M		
Comments:					
Operator:	IIS	**Sample weight:**	0.0954 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	200.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	60.0 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	06/23/2008 16:22
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
4.8882e-02	4.9055	8.383E+00
8.0069e-02	5.5395	1.257E+01
1.0526e-01	6.0098	1.566E+01

Area = 2.650E+01 m²/g

Slope = 1.293E+02

Y - Intercept = 2.109E+00

Correlation Coefficient = 0.999673

C = 6.232E+01

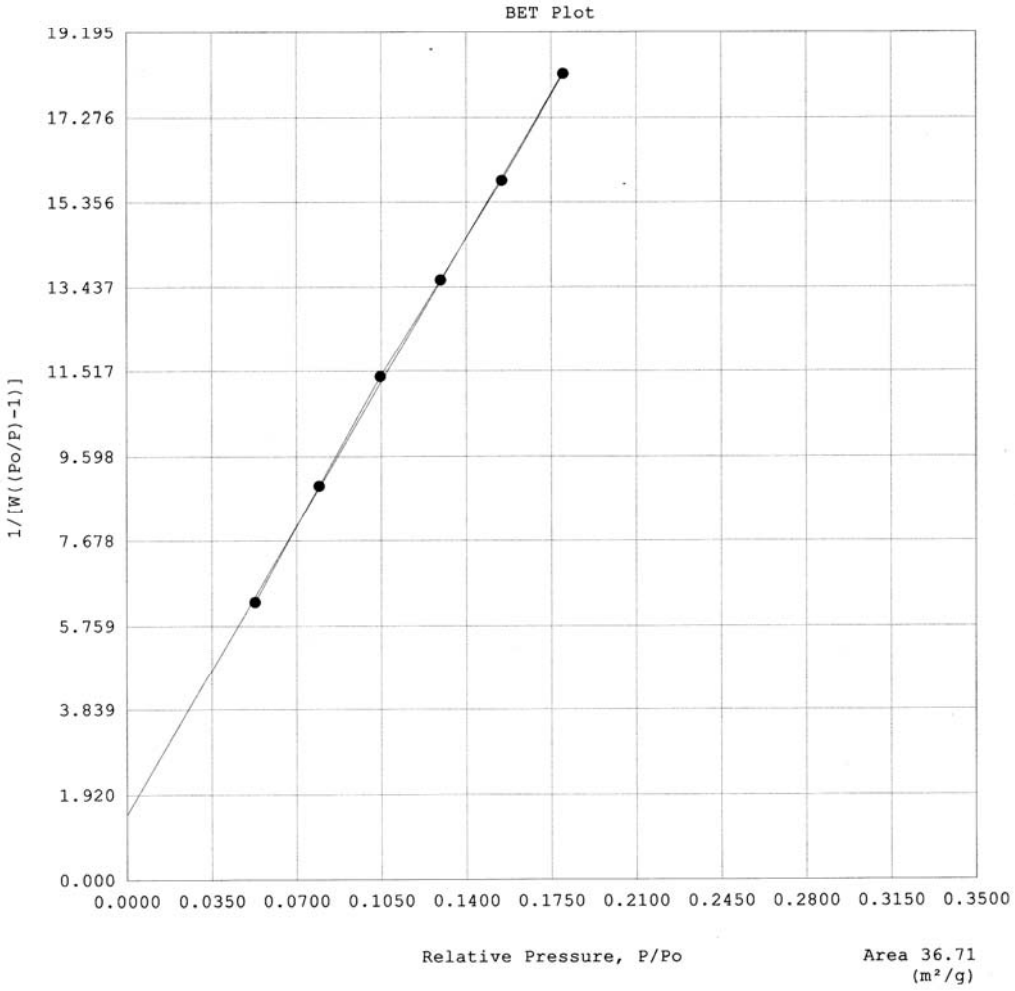
BET analysis of acid treated Green Bentonite

09/25/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS892503GBAT7%8M.raw				
Sample ID:	GBAT7%8M	**Description:**	GBAT7%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1666 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	57.2 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/25/2008 13:54
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.2985e-02	7.1079	6.298E+00
7.9419e-02	7.7287	8.931E+00
1.0471e-01	8.2143	1.139E+01
1.2952e-01	8.7600	1.359E+01
1.5481e-01	9.2390	1.586E+01
1.8002e-01	9.6255	1.825E+01

Area = 3.671E+01 m²/g

Slope = 9.339E+01

Y - Intercept = 1.468E+00

Correlation Coefficient = 0.999781

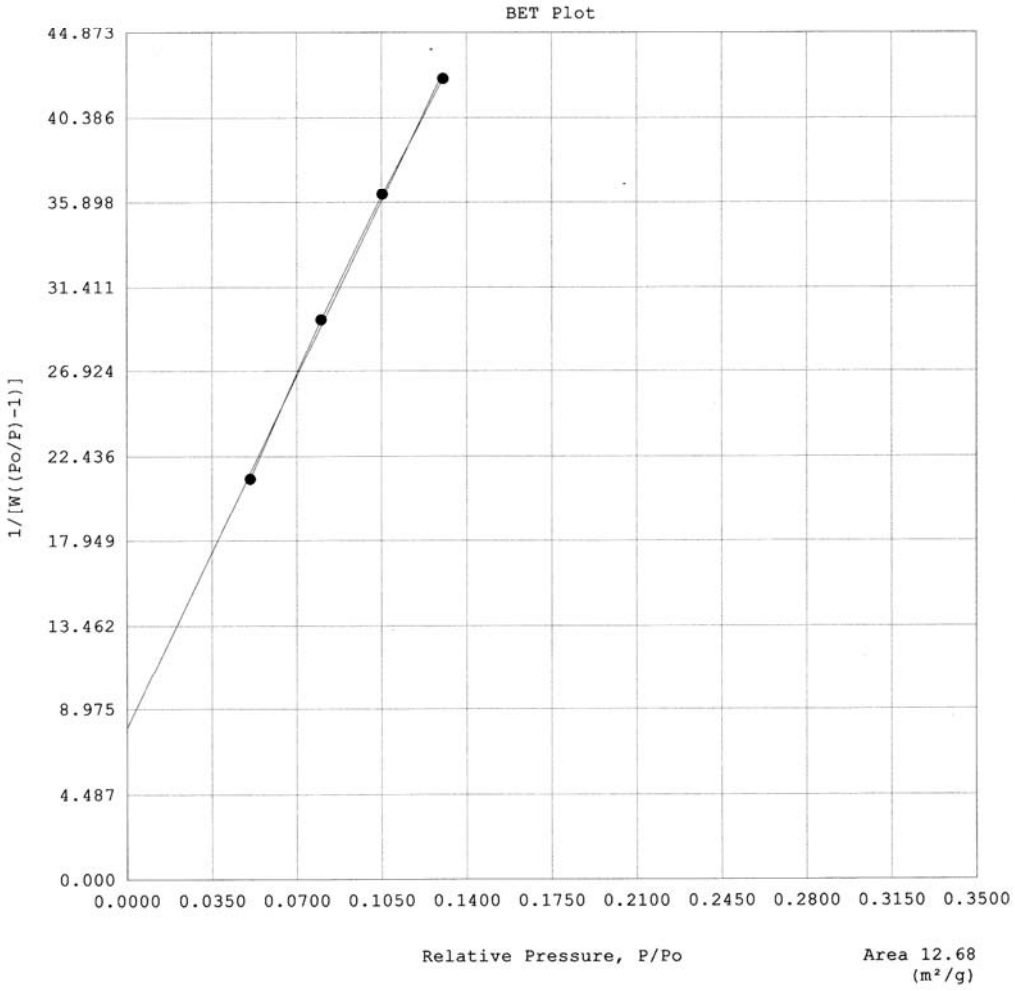
BET analysis of lime treated Green Bentonite

09/25/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS892501GBLT10%8M.raw				
Sample ID:	GBLT10%8M	**Description:**	GBLT10%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1697 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	59.1 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/25/2008 11:24
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.0964e-02	2.0218	2.125E+01
8.0170e-02	2.3486	2.969E+01
1.0538e-01	2.5940	3.633E+01
1.3041e-01	2.8285	4.242E+01

Area = 1.268E+01 m²/g

Slope = 2.666E+02

Y - Intercept = 7.972E+00

Correlation Coefficient = 0.999219

C = 3.444E+01

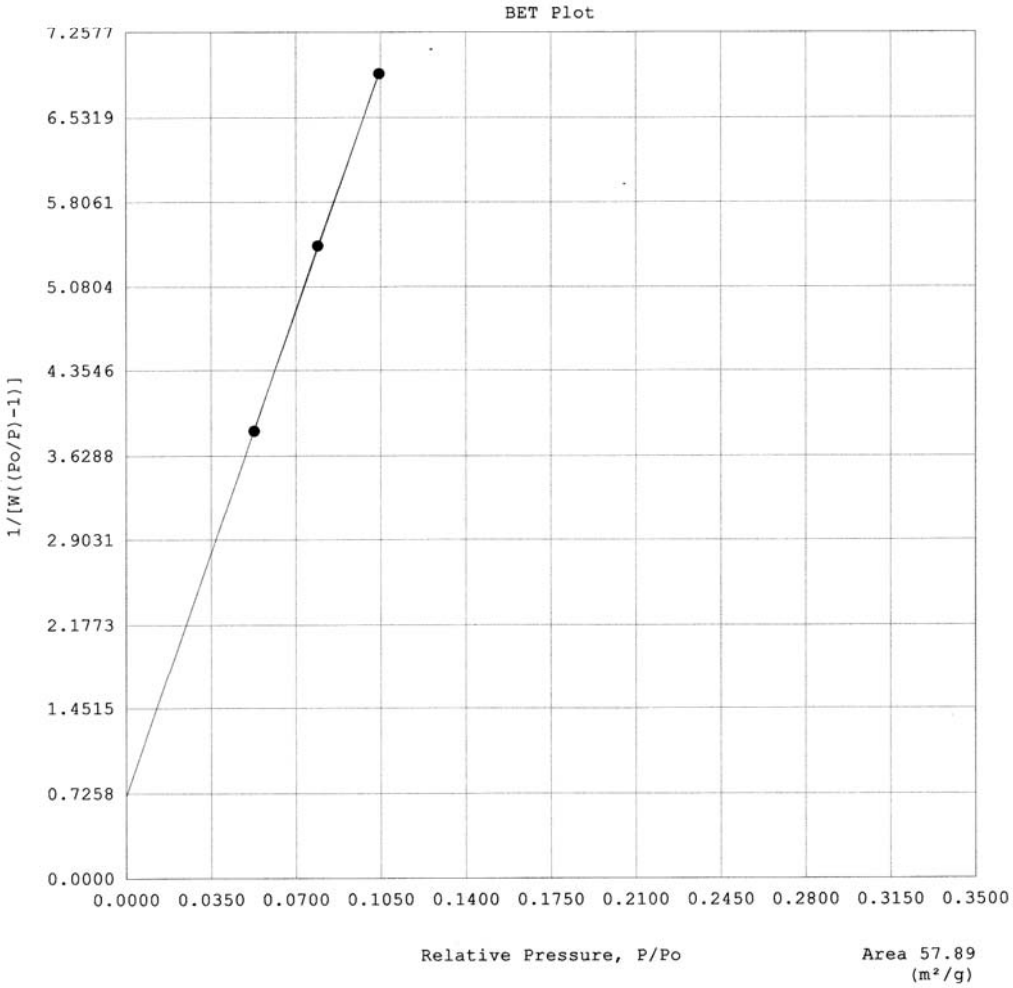
BET analysis of untreated Laterite Clay

06/23/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS862302LCUT 0% 4M.raw				
Sample ID:	LCUT 0% 4M	**Description:**	LCUT 0% 4M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1285 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	200.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	56.1 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	06/23/2008 17:32
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.2915e-02	11.6396	3.841E+00
7.9081e-02	12.6552	5.429E+00
1.0439e-01	13.5149	6.901E+00

Area = 5.789E+01 m²/g

Slope = 5.945E+01

Y - Intercept = 7.056E-01

Correlation Coefficient = 0.999922

C = 8.526E+01

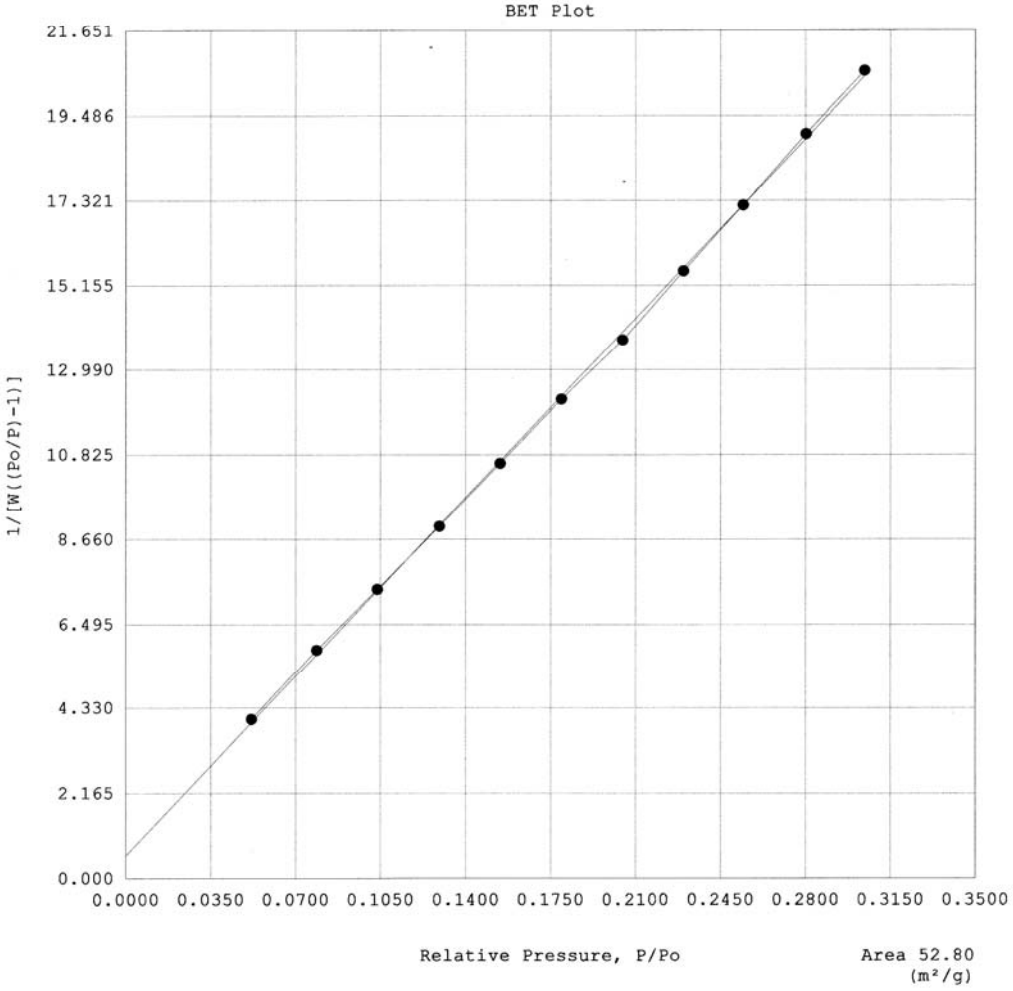
BET analysis of acid treated Laterite Clay

09/17/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS891701LCAT7%8M.raw				
Sample ID:	LCAT7%8M	**Description:**	LCAT7%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1552 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	59.8 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/17/2008 10:38
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.1959e-02	10.8391	4.046E+00
7.8796e-02	11.7231	5.838E+00
1.0382e-01	12.5374	7.393E+00
1.2928e-01	13.2152	8.990E+00
1.5436e-01	13.7761	1.060E+01
1.7962e-01	14.3189	1.223E+01
2.0475e-01	14.9783	1.375E+01
2.2983e-01	15.3876	1.552E+01
2.5439e-01	15.8726	1.720E+01
2.8031e-01	16.3800	1.902E+01
3.0446e-01	16.9858	2.062E+01

Area = 5.280E+01 m²/g

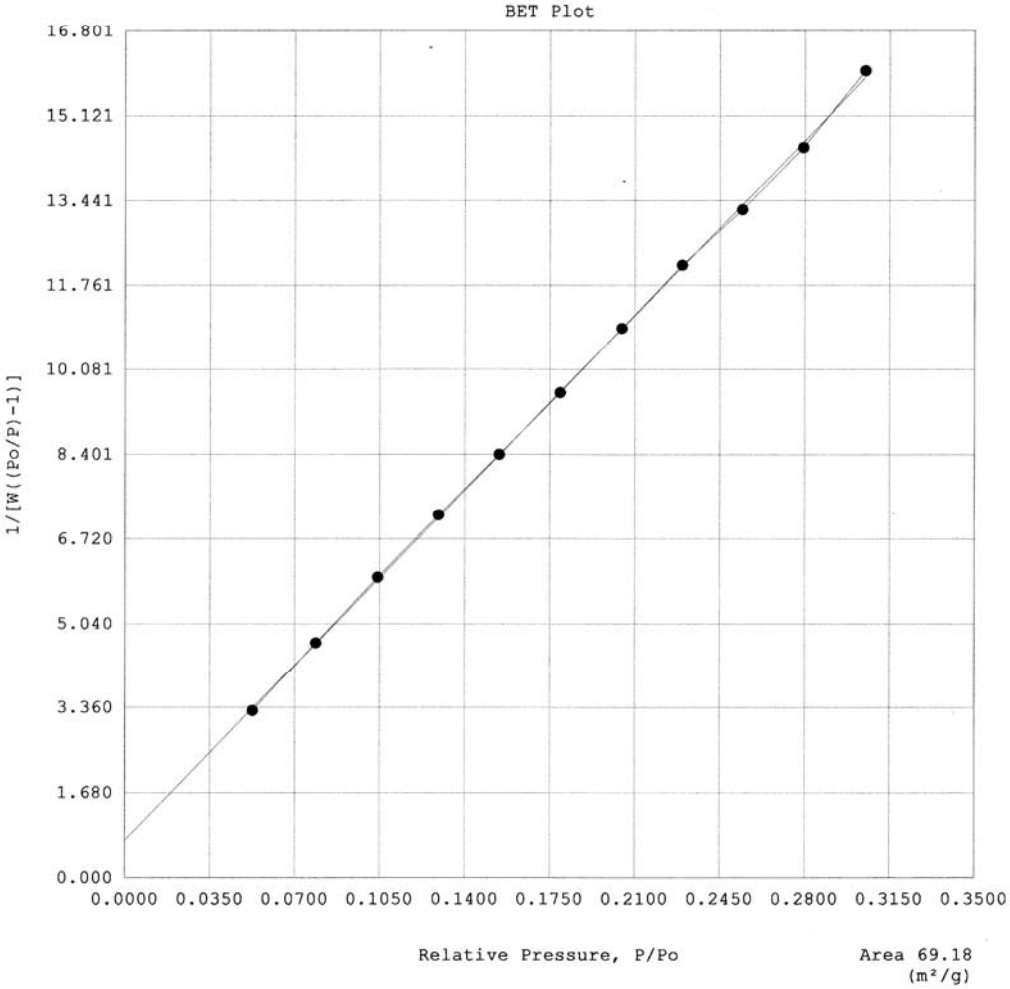
BET analysis of lime treated Laterite Clay

09/18/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS891801LCLT7%8M.raw				
Sample ID:	LCLT7%8M	**Description:**	LCLT7%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1241 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	61.4 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/18/2008 10:41
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.2696e-02	13.4924	3.299E+00
7.8797e-02	14.6864	4.660E+00
1.0429e-01	15.6266	5.962E+00
1.2935e-01	16.5143	7.198E+00
1.5431e-01	17.3784	8.401E+00
1.7942e-01	18.1911	9.617E+00
2.0471e-01	18.8953	1.090E+01
2.2963e-01	19.6185	1.216E+01
2.5440e-01	20.5837	1.326E+01
2.7950e-01	21.4054	1.450E+01
3.0505e-01	21.9491	1.600E+01

Area = 6.918E+01 m²/g

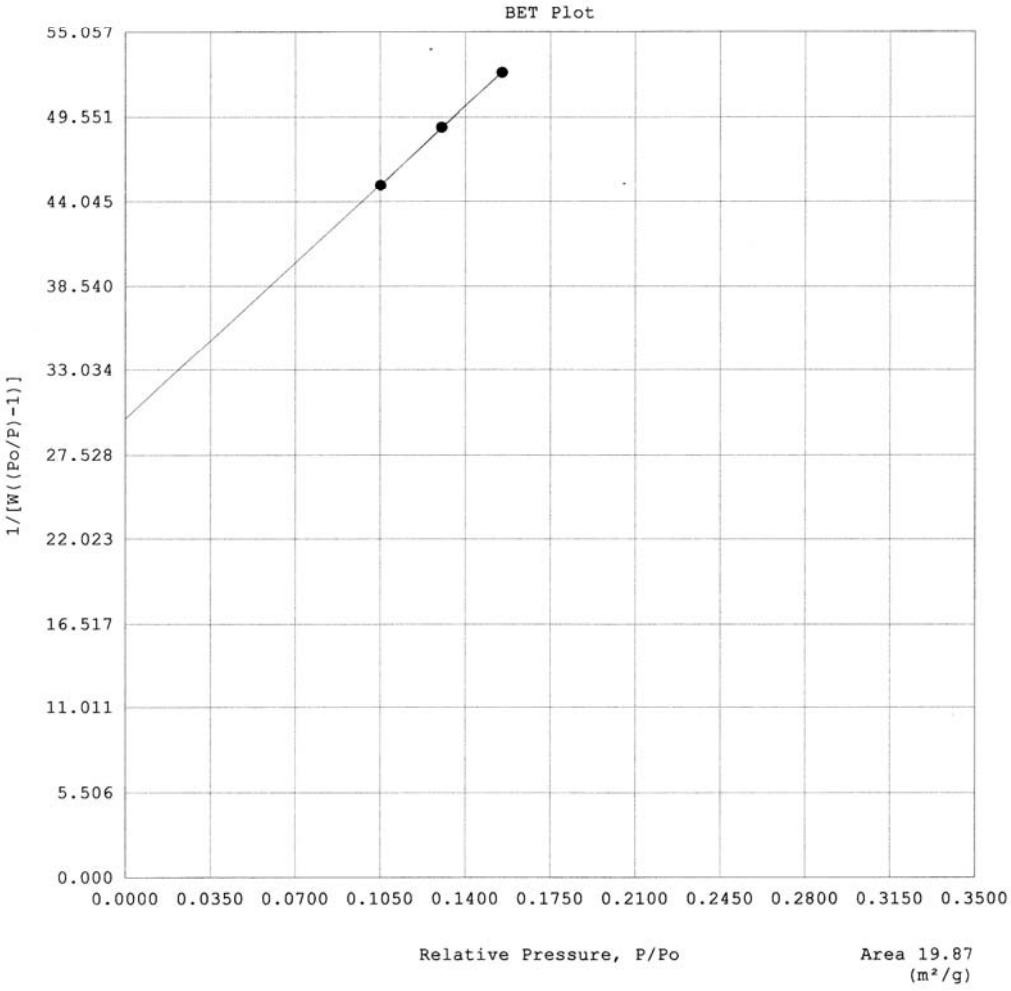
BET analysis of untreated White Kaolin

06/10/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS861002WKUT 0% 4M.raw				
Sample ID:	WKUT 0% 4M	**Description:**	WKUT 0% 4M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1124 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	200.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	63.6 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	06/10/2008 11:12
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
1.0521e-01	2.0848	4.513E+01
1.3031e-01	2.4526	4.888E+01
1.5523e-01	2.8057	5.240E+01

Area = 1.987E+01 m²/g

Slope = 1.454E+02

Y - Intercept = 2.986E+01

Correlation Coefficient = 0.999864

C = 5.870E+00

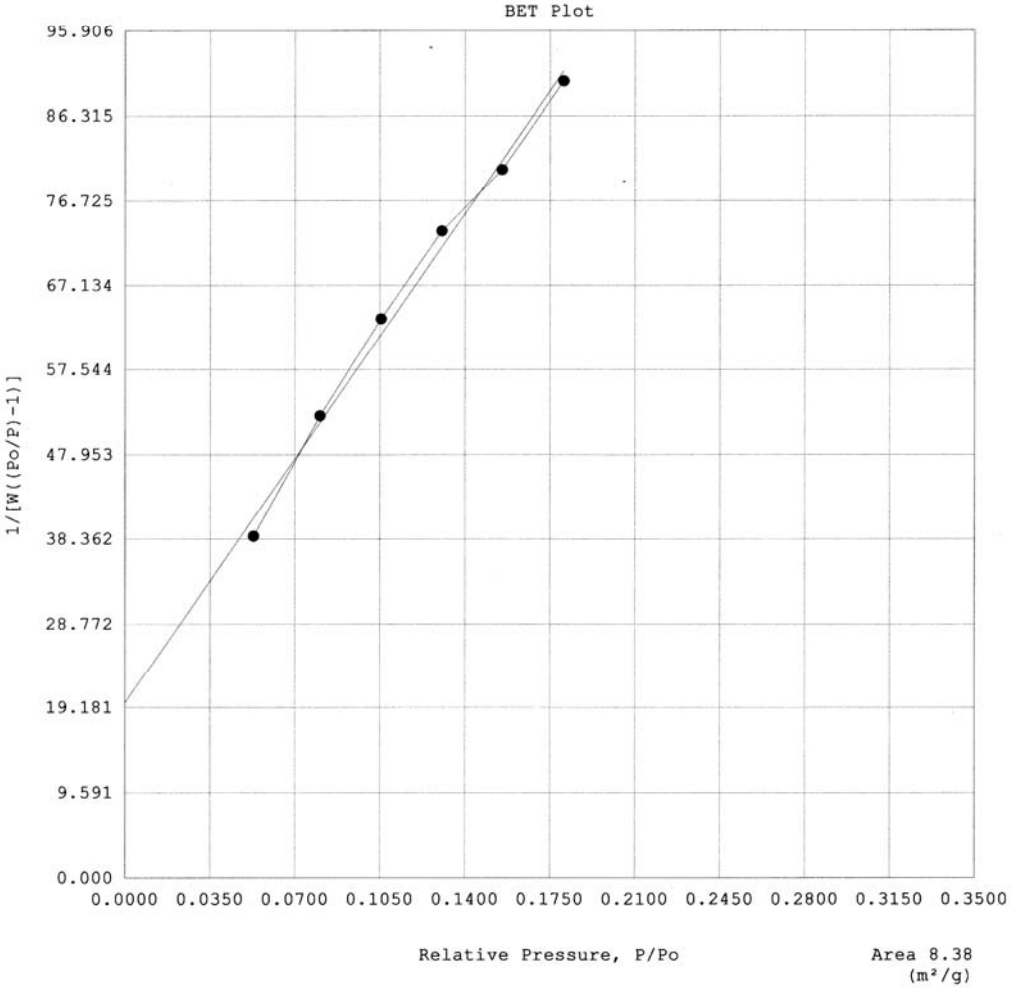
BET analysis of acid treated White Kaolin

09/24/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS892401JME-HP-5VST33-100.raw				
Sample ID:	WKAT5%8M	**Description:**	WKAT5%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1266 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	68.5 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/24/2008 11:36
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.3100e-02	1.1602	3.867E+01
8.0458e-02	1.3381	5.232E+01
1.0561e-01	1.4918	6.333E+01
1.3061e-01	1.6407	7.326E+01
1.5541e-01	1.8341	8.028E+01
1.8079e-01	1.9579	9.019E+01

Area = 8.376E+00 m²/g

Slope = 3.960E+02

Y - Intercept = 1.975E+01

Correlation Coefficient = 0.996174

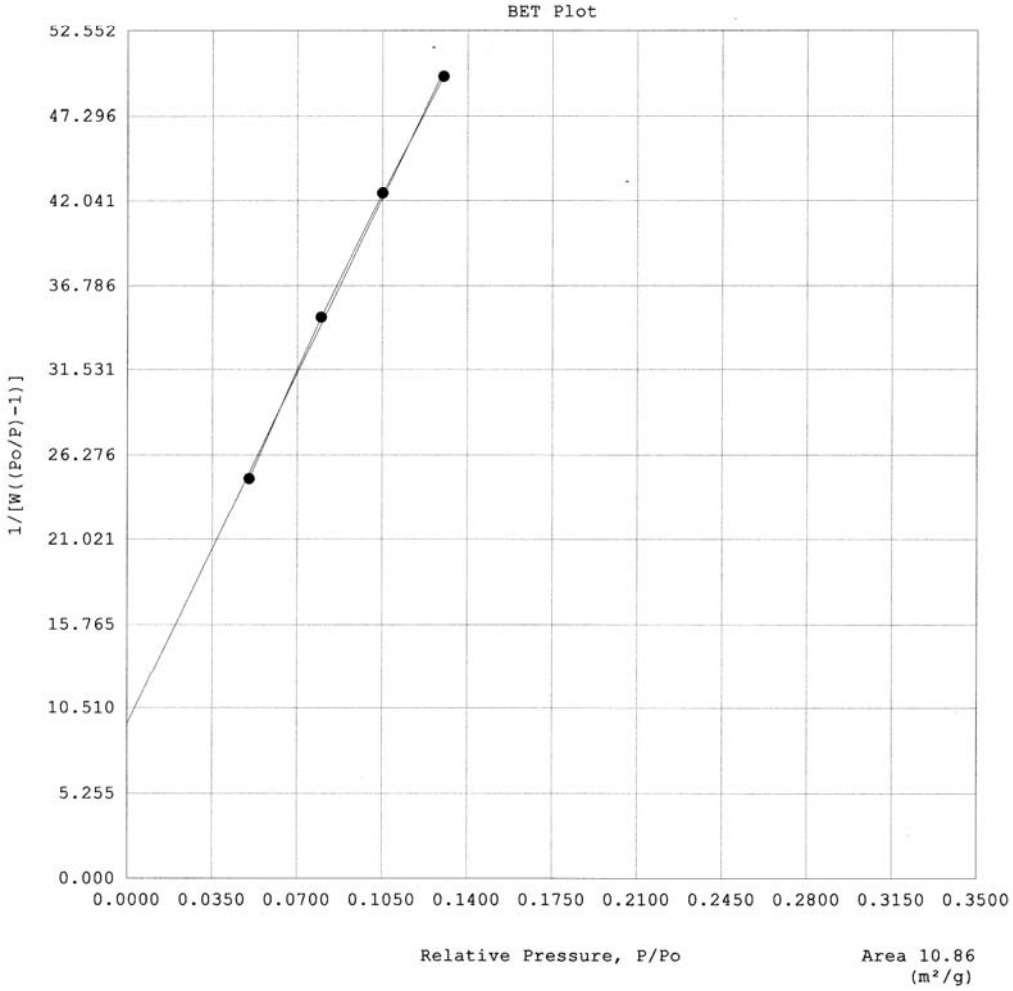
BET analysis of lime treated White Kaolin

09/19/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS891902WKLT5%8M.raw				
Sample ID:	WKLT5%8M	**Description:**	WKLT5%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.2204 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	59.0 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/19/2008 12:26
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.0261e-02	1.7063	2.481E+01
7.9911e-02	1.9944	3.484E+01
1.0512e-01	2.2103	4.252E+01
1.3018e-01	2.4095	4.970E+01

Area = 1.086E+01 m²/g

Slope = 3.112E+02

Y - Intercept = 9.534E+00

Correlation Coefficient = 0.999237

C = 3.364E+01

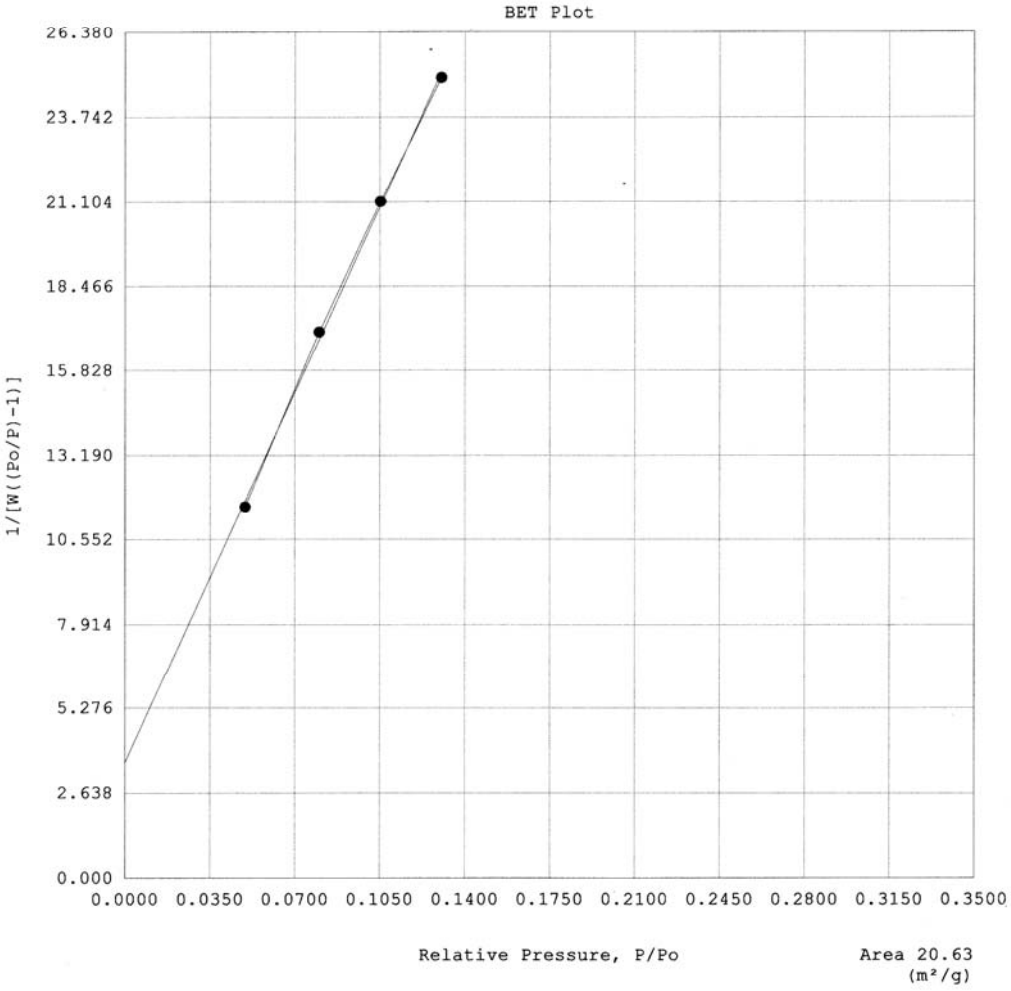
BET analysis of untreated Pink Soil

06/12/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS861202PSUT 0% 4M.raw				
Sample ID:	PSUT 0% 4M	**Description:**	PSUT 0% 4M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1186 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	200.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	59.8 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	06/12/2008 18:02
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
4.9557e-02	3.6015	1.158E+01
8.0097e-02	4.0884	1.704E+01
1.0537e-01	4.4633	2.111E+01
1.3040e-01	4.8087	2.495E+01

Area = 2.063E+01 m²/g

Slope = 1.652E+02

Y - Intercept = 3.576E+00

Correlation Coefficient = 0.999333

C = 4.721E+01

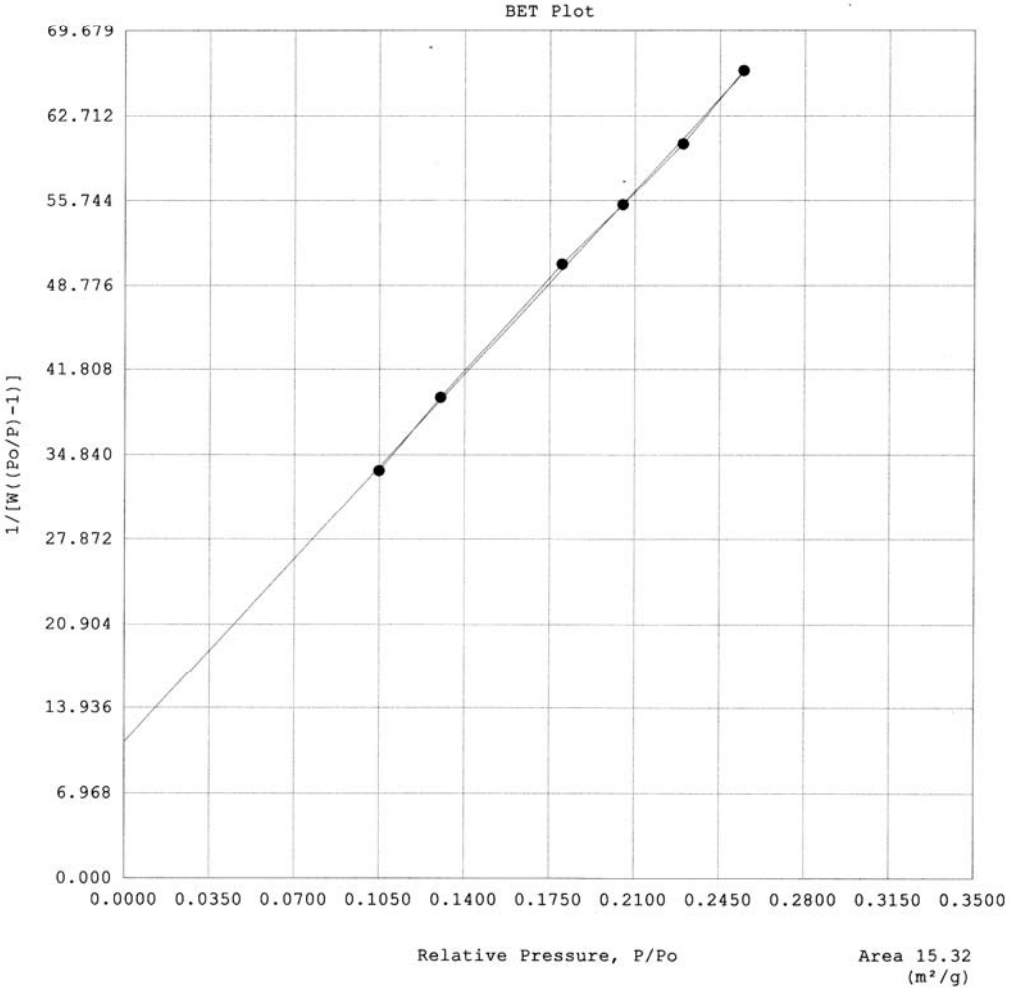
BET analysis of acid treated Pink Soil

09/19/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS891901PSAT5%8M.raw				
Sample ID:	PSAT5%8M	**Description:**	PSAT5%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1457 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	62.6 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/19/2008 11:12
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
1.0500e-01	2.7993	3.353E+01
1.3026e-01	3.0332	3.951E+01
1.8010e-01	3.4787	5.052E+01
2.0513e-01	3.7261	5.541E+01
2.2989e-01	3.9525	6.043E+01
2.5482e-01	4.1230	6.636E+01

Area = 1.532E+01 m²/g

Slope = 2.162E+02

Y - Intercept = 1.113E+01

Correlation Coefficient = 0.999663

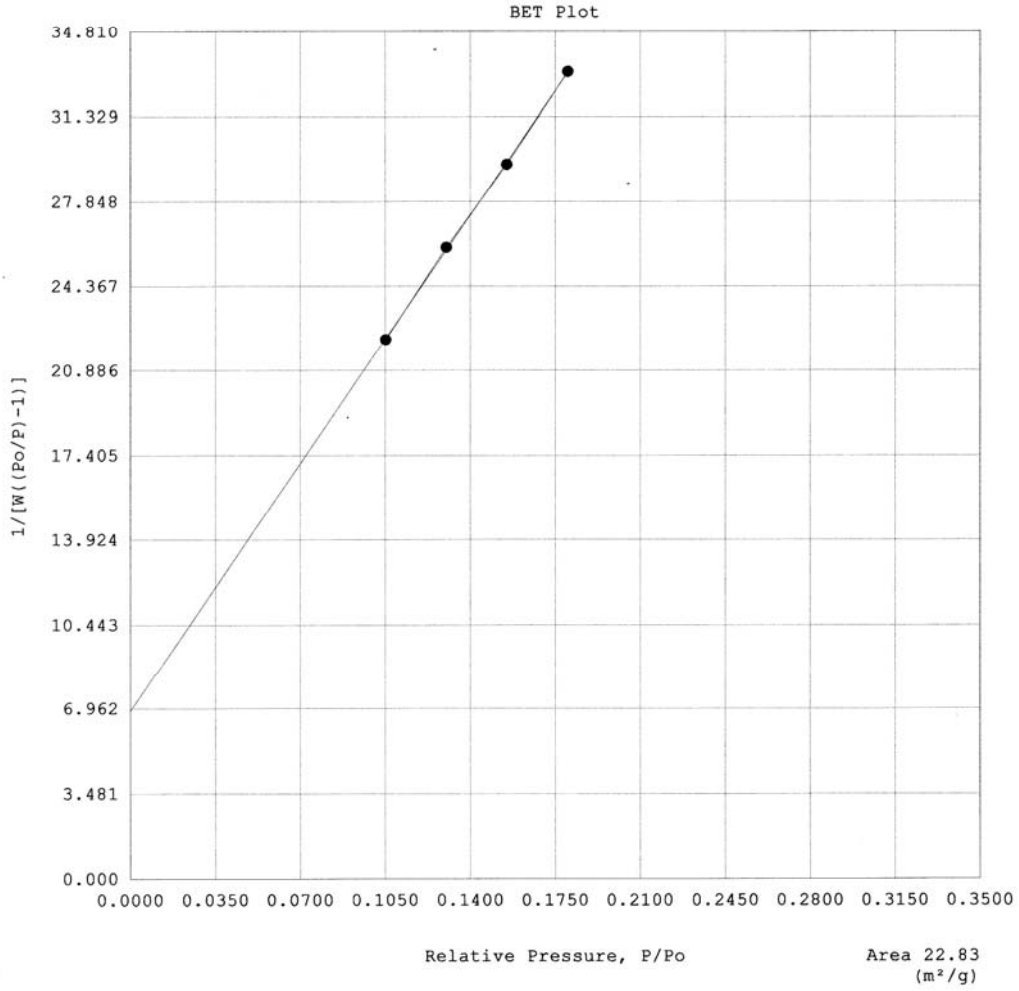
BET analysis of lime treated Pink Soil

09/18/2008

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.51

File name:	C:\QCdata\PhysData\AS891802PSLT5%8M.raw				
Sample ID:	PSLT5%8M	**Description:**	PSLT5%8M		
Comments:					
Operator:	IIS	**Sample weight:**	0.1072 g		
Analysis gas:	Nitrogen	**X sect. area:**	16.2 Å²/molec	**Non-ideality:**	6.58e-05
Adsbate (DRP):	Nitrogen	**Bath Temp.:**	77.30		
Outgas Temp:	300.0 °C	**Outgas Time:**	20.0 hrs	**Analysis Time:**	63.8 min
P/Po tolerance:	1	**Equil. time:**	1	**End of run:**	09/18/2008 12:09
Station #:	1	**PC sw. version:**	1.51	**TempComp:**	Off

A —●— BF ——



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
1.0532e-01	4.2496	2.216E+01
1.3026e-01	4.6178	2.595E+01
1.5513e-01	4.9997	2.939E+01
1.8032e-01	5.3093	3.315E+01

Area = 2.283E+01 m²/g

Slope = 1.457E+02

Y - Intercept = 6.867E+00

Correlation Coefficient = 0.999846

C = 2.221E+01

UNIVERSITI TEKNOLOGI MALAYSIA

BORANG PENGESAHAN
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK : THE NANOSTRUCTURE STUDY ON THE MECHANISM OF LIME STABILIZED SOIL

Saya PROF. DR KHAIRUL ANUAR B. KASSIM
(HURUF BESAR)

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